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Performance Test Results and Comparative Data for Designated Reference Methods for Carbon Monoxide

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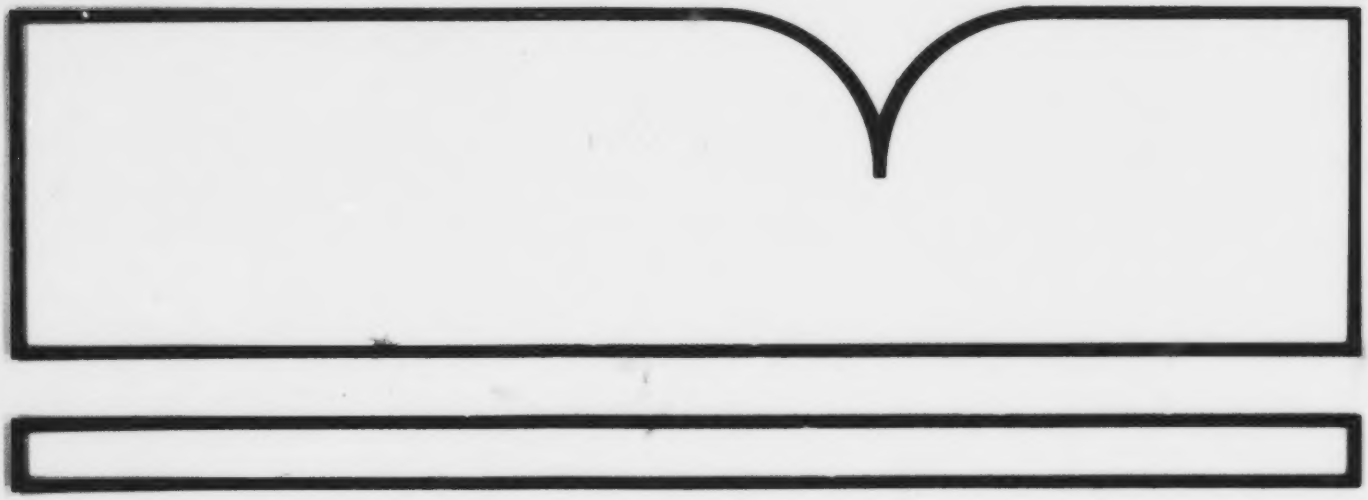

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Performance Test Results and Comparative Data for Designated Reference Methods for Carbon Monoxide

by

Raymond M. Michie, Jr.
John A. Sokash
Dave-Paul Dayton
Carol R. Sutcliffe
Environmental Quality Assurance Department
Research Triangle Institute
Research Triangle Park, NC 27709

Frank F. McElroy
Vinson L. Thompson
Methods Standardization Branch
Quality Assurance Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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EPA Project Officers: Frank F. McElroy, Vinson L. Thompson
Quality Assurance Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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The U.S. Environmenental Protection Agency designates specific ambient monitoring methods and analyzers as reference or equivalent methods acceptable for use in certain required monitoring. Such designation is based on performance testing of the analyzer by the manufacturer (or other applicant) prior to designation. After designation, EPA carries out further tests of the analyzer, including performance tests as well as comparative tests to evaluate the performance, reliability, and operational peculiarities of the analyzer with respect to other analyzers monitoring the same pollutant.

This report summarizes both the manufacturer's predesignation test results and the available EPA postdesignation test results for currently designated carbon monoxide analyzers. Manufacturer's predesignation test results are presented for nine analyzers, and all test results met or exceeded the required specifications. EPA postdesignation performance test results are presented for eight analyzers, and similarly, all test results met or exceeded the specifications. EPA post-designation comparative test results are presented for five analyzers, with the results indicating that the analyzers tested were stable and reliable and demonstrated a high degree of comparability.

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, has responsibility for: assessing environmental monitoring technology and systems; implementing Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Assessment of environmental monitoring technology is performed in part by the Quality Assurance Division. Through the Equivalency Testing Program, automated analyzers are evaluated to ensure that specified performance criteria are met. This document is one in a series of four that summarizes performance test results and comparative data obtained during analyzer evaluations. The series will document evaluations of analyzers that monitor ambient air for ozone, oxides of nitrogen, sulfur dioxide, and carbon monoxide.

ABSTRACT

Under Part 53 of Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency designates specific ambient monitoring methods and analyzers as reference or equivalent methods acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring. Such designation requires that extensive performance testing of the analyzer be carried out by the manufacturer (or other applicant) prior to designation. After designation, EPA carries out further tests of the analyzer. These EPA tests include performance tests as well as comparative tests to evaluate the performance, reliability, and operational peculiarities of the analyzer with respect to other analyzers monitoring the same pollutant.

This report summarizes both the manufacturer's predesignation test results and the available EPA postdesignation test results for currently designated carbon monoxide analyzers. Manufacturer's predesignation test results are presented for nine analyzers. The manufacturer's tests were conducted according to procedures presented in 40 CFR Part 53 and all test results met or exceeded the specifications contained therein. EPA Phase I postdesignation test results are presented for eight analyzers. These tests were conducted according to an abridged version of the 40 CFR Part 53 procedures. Again, all test results met or exceeded the CFR specifications. EPA Phase II postdesignation test results are presented for five analyzers. Although these tests were primarily comparative in nature with no formal performance specifications applied to the data, the results indicated that the analyzers tested were stable and reliable and demonstrated a high degree of comparability among themselves.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

CFR	--Code of Federal Regulations
DAMDF	--Durham Air Monitoring Demonstration Facility
EMSL	--Environmental Monitoring Systems Laboratory
EPA	--U.S. Environmental Protection Agency
GFC	--gas filter correlation
h	--hour
Hz	--hertz (frequency in cycles per second)
IR	--infrared
kPa	--kilo pascal
L	--liter
LDL	--lower detectable limit
m	--meter
mm	--millimeter
MSB	--Methods Standardization Branch
MDL	--minimum detectable limit
NAMS	--National Air Monitoring Station
NBS	--National Bureau of Standards
NDIR	--nondispersive infrared
ppm	--parts per million
PSD	--prevention of significant deterioration
psig	--pounds per square inch, gauge
QAD	--Quality Assurance Division
SLAMS	--State and Local Air Monitoring Station
SRM	--standard reference material
µm	--micrometer
URL	--upper range limit
Vac	--volts, alternating current

SYMBOLS

~	--approximately
CO	--carbon monoxide
CO_2	--carbon dioxide
H_2O	--water
$H_2O(v)$	--water vapor
NO_x	--oxides of nitrogen
NO_2	--nitrogen dioxide
O_3	--ozone
SO_2	--sulfur dioxide

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SECTION 1

INTRODUCTION

Under Part 53 of Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency (EPA) designates specific ambient monitoring methods and analyzers as acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring, among other monitoring applications. These methods are designated as reference methods or equivalent methods, depending on whether or not the method employs a particular measurement principle and calibration procedure specified for each pollutant in 40 CFR Part 50. A list of all currently designated methods is available from the Quality Assurance Division (QAD) or from the Quality Control Coordinator at any EPA Regional Office.

Commercial analyzer models are designated as reference or equivalent methods based on an application submitted by the manufacturer (or other applicant). This application must show that a test analyzer representative of the analyzer model meets the following criteria:

1. It has been tested according to specific test procedures prescribed in 40 CFR Part 53;

2. It meets prescribed minimum performance specifications; and

3. It meets certain other requirements such as having a suitable calibration procedure and an adequate operation and instruction manual.

Any designated analyzer model should meet the requirements mentioned above. However, these analyzer models may differ considerably in design, features, reliability, measurement principle, ease of operation, and level of performance above the required minimum. These factors allow for intelligent selection of the best or most appropriate analyzer for a particular application.

The Methods Standardization Branch (MSB) of the Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, NC, is responsible for EPA's reference and equivalent method designation program for ambient air monitoring methods. In this capacity, MSB acquires performance data and other information on these methods, particularly on the various commercial analyzer models that have been designated as reference or equivalent methods.

To summarize this information and make it available to those who may find it beneficial in selecting analyzers, MSB, with the assistance of the Research Triangle Institute (RTI), has prepared this report on designated methods for carbon monoxide. Previous reports have discussed designated methods for ozone and sulfur dioxide.

The information presented in this report is derived from the following sources:

1. The predesignation test data submitted by the applicant,

2. Postdesignation tests conducted by MSB,

3. Reports or comments from analyzer users, and

4. Other pertinent information as needed.

The predesignation test data were extracted from the application for designation submitted by the applicant (usually the analyzer manufacturer) and were thus obtained from tests conducted at the applicant's own laboratory or test site. These tests must be conducted in accordance with the explicit test procedures specified in 40 CFR Part 53. Results must then be calculated and interpreted according to the prescribed specifications.

The postdesignation tests conducted by MSB are part of an ongoing postdesignation test program and may include one or more of the following types:

1. Phase I tests are laboratory performance tests similar to the predesignation tests required by 40 CFR Part 53;

2. Phase II tests simulate actual use conditions and serve to intercompare designated methods; and

3. Phase III tests are special purpose tests for specific analyzers and are used when unique needs or circumstances arise.

Postdesignation test results are the major source of information in this report and are described in detail in Section 2. The tests are conducted either by Quality Assurance Division personnel or by a contractor, under QAD direction, who has no contractual or financial association with any commercial manufacturers of designated analyzers. Because of resource limitations, there may be substantial delays in completing the postdesignation tests of an analyzer model following its designation as a reference or equivalent method.

The information in this report is based on files maintained by MSB for each designated method. MSB encourages analyzer users to submit comments that might be of interest to others using or contemplating purchase of a designated analyzer. Such comments, particularly negative comments, are more valuable if they are accompanied by supporting data, records, or other documentation. Pertinent information from other sources, such as other EPA groups, testing laboratories, and manufacturers will also be included when available. Publication of an updated report will be considered whenever significant new information is available.

Additional information on any aspect of the report may be obtained from MSB. The report is not intended to recommend or endorse any particular analyzer over others. MSB welcomes any comments on the usefulness of these reports or suggestions for improvement. Remarks may be mailed to the address on the front page or made by phone to any of the following numbers:

Commercial:	(919)	541-2622
	(919)	541-3791
FTS:		629-2622
		629-3791

SECTION 2

POSTDESIGNATION TESTING

Because the primary predesignation testing of an analyzer is carried out by the manufacturer or other applicant, it is EPA's general policy to perform followup performance tests on the analyzer after designation. These tests are referred to as postdesignation tests and are of three types: Phase I, Phase II, and Phase III. Phase I and II tests are described below. Phase III tests include any special tests or special circumstances not covered by Phase I and II and are conducted only when deemed necessary or appropriate.

The postdesignation tests are usually carried out after designation on an analyzer purchased by EPA through normal procurement procedures. Occasionally, an analyzer purchased prior to designation is returned to the manufacturer for upgrading to designated status. Commercially unavailable analyzers are borrowed for the tests. The manufacturer is always notified of the testing to be done and of the fact that the test analyzer obtained is assumed to be representative of the model. Because of the complex nature of most analyzers, variability in performance from one instrument to another can be expected. Even though all analyzers must be within the required specifications, this potential variability must be kept in mind when the test results in this report are considered and compared with those of other analyzers.

PHASE I TESTS

General Description

Phase I tests are laboratory performance tests that are conducted in accordance with the same test procedures and specifications required for the applicant's predesignation tests. The one exception is that fewer trials (usually four) are performed for each test parameter to reduce costs. All calibrations, test apparatus, pollutant standards, test procedures, test atmospheres, and test documentation are as specified in 40 CFR Part 53. An individual report containing more detailed information on the Phase I test for each analyzer tested is available from MSB.

Analyzers to be Phase I tested are set up and allowed to operate for several weeks prior to actual testing. During this startup period, preliminary calibrations and linearity checks are performed to verify proper operation. In the event that unusual behavior such as nonlinearity or inoperability due to a major malfunction is identified, the manufacturer is notified. The manufacturer is encouraged to become involved throughout the

startup period so that potential problems may be identified prior to testing. If a failure occurs during testing, the manufacturer is notified and given the opportunity to repair the analyzer. At the conclusion of the test, all failures and manufacturer involvement are documented and reported.

Data Interpretation

The Phase I test results for each analyzer are shown in Tables 3 through 11 along with the EPA performance specifications and the applicants' own predesignation test data (as submitted in the equivalency application). The results reported are averages of several trials for each parameter (usually four trials for the EPA Phase I data and seven for the applicant's predesignation data). The test results must generally be less than (or within) the EPA performance specifications shown for an analyzer to achieve designation, and, except for the lower detectable limit, these results are comparable in a relative sense from one instrument to another. The manufacturer's advertised or claimed performance specifications, however, may not be directly comparable to the test data or to other analyzers since manufacturers may choose to define their performance specifications, or how they are measured, differently. The various EPA performance parameters are described briefly below along with pertinent comments. See 40 CFR Part 53 for the formal definitions of the performance parameters and the prescribed test procedure for each.

Noise--

Noise refers to short-term deviations in the analyzer output that are not caused by changes in the input concentration. Noise is measured at both 0 percent and 80 percent of the upper range limit and is the standard deviation of 25 readings taken at 2-minute intervals. Normally, this value will be slightly less than the average absolute deviation from the mean value and is usually much less than the peak-to-peak noise.

Lower Detectable Limit--

The lower detectable limit (LDL) is the smallest pollutant concentration that produces an output change of at least twice the noise level. The test does not determine the actual LDL; it only verifies that the output signal at an input concentration of 1.0 ppm is at least two times the 0-ppm noise level. Therefore, the value reported is usually close to 1.0 ppm and must be greater than twice the noise level. An output signal significantly lower than 1.0 ppm may indicate a nonapparent negative zero offset or other low-level response problems.

Interference Equivalent--

The interference equivalent is the relative degree of unwanted response caused by compounds other than carbon monoxide present in the ambient air sample. The reported values should not be interpreted as the actual error to be expected in ambient measurements because the test concentrations of most of the interferents are higher than those normally encountered in ambient air. However, the values for water and CO_2 do represent the approximate error that may result when the calibration gases are dry and/or free of CO_2.

Zero Drift (12 h)--

The 12-h zero drift is the maximum change in continuous output response to zero input concentration over a 12-h period of unadjusted operation. The 12-h zero drift includes any peak-to-peak noise component, so it may be higher than the 24-h zero drift.

Zero Drift (24 h)--

The 24-h zero drift is the net change in response to zero input concentration between two points in time ~24 h apart during unadjusted analyzer operation. It includes changes in ambient temperature, line voltage, or both. The 24-h zero drift tends to be sometimes positive, sometimes negative; hence the average would be misleadingly low. Therefore, the average of the absolute values of the analyzer's daily drift is reported in Tables 3 through 11 as a more meaningful value.

Span Drift (20% URL)--

The span drift at 20 percent upper range limit (URL) is the net change in response to an input concentration of ~20 percent of the URL between two points in time ~24 h apart during unadjusted analyzer operation and including changes in ambient temperature, line voltage, or both. Because of the 20-percent URL concentration level, the reported value represents a combination of both zero drift and span drift over the period. The average of the absolute values is reported.

Span Drift (80% URL)--

In the test of span drift at 80 percent URL, an input concentration of ~80 percent URL is used. The 80-percent URL span drift is calculated without a correction for zero drift; therefore it may be higher or lower than the actual change in the slope of the calibration curve. Again, the average of the absolute values of the individual daily results is reported.

Lag Time--

Lag time is the time required to observe the first change in response resulting from a sudden change in input concentration.

Rise Time--

Rise time is the time (not including the lag time) required for the response to reach 95 percent of its final value after a sudden increase in the input concentration.

Fall Time--

Fall time is the time (not including lag time) required for the response to decrease to 5 percent of its previous value when the input concentration is suddenly changed to 0 ppm.

Long lag, rise, or fall times generally do not adversely affect measurements expressed as hourly averages and may even be beneficial where concentrations fluctuate rapidly. However, long response times may be an annoyance or source of error during calibration and zero and span drift adjustment.

Precision--

Precision is the variation in the response value to six repeated measurements of the same upscale pollutant concentration, approached alternately from lower and higher concentrations. The reported precision is a measure of the repeatability of the analyzer and is determined at both 20 and 80 percent of the URL.

PHASE II TESTS

General Description

Phase II tests are intended to test analyzers in a more or less typical ambient monitoring configuration where their stability, reliability, general performance, and operational peculiarities can be observed, recorded, and compared. The tests are conducted simultaneously on a group of analyzers during a period of several months. All analyzers measure the same pollutant in the ambient air, which is sampled from a common manifold. The ambient pollutant concentrations are sometimes augmented in the manifold with artificially generated pollutant to increase the concentration readings.

Unless otherwise specified, the Phase II tests are carried out at EPA's Durham Air Monitoring Demonstration Facility (DAMDF) in an urban/industrial/commercial area of Durham, NC. Ambient air samples for the analyzers are drawn from an intake on the building roof and distributed by an all-glass, power-ventilated manifold system. Pollutant levels are augmented, when appropriate. During such augmentation, however, all sample air contains at least 90 percent unaltered ambient air. The analyzers' inlets are connected to the manifold via Teflon® particulate filters and either 3-mm (1/8-in) or 6-mm (1/4-in) Teflon® tubing, depending on the analyzer flow rate. The sample lines are kept as short as practical.

All test analyzers are installed, calibrated, operated, and maintained in accordance with the manufacturer's operation/instruction manual and good monitoring practice. Analyzers receive a multipoint calibration initially and once per month during the test period. Two-point zero and span checks are made two or three times per week, with zero adjustments only if the zero response is not within ±3 percent of full-scale response from nominal, and span adjustments only if the span (slope of calibration curve) changes by more than ±7 percent from nominal.

Zero air is obtained from filtered ambient air by appropriate drying and chemical scrubbing. Catalytic oxidation is used to remove organic compounds and carbon monoxide. Calibration and span gases are obtained by techniques such as dilution of high concentration cylinder gases, permeation devices, and gas phase titration. Ozone concentrations are generated by ultraviolet radiation and are traceable to a UV standard; all other pollutant concentrations are traceable to National Bureau of Standards Standard Reference Materials (NBS-SRMs).

Analyzer readings are recorded at 1-min intervals using a Monitor Labs 9300 data acquisition system. One-hour averages (50-min minimum) are automatically calculated and transferred to magnetic tape. Zero and span responses are also recorded on the tape. The tapes are read into a Hewlett-Packard 9831A or 9845A Desk Top computer for verification, editing, corrections as necessary, and calculation of the various statistical comparisons.

Data Interpretation

Phase II testing is primarily intended to be comparative in nature. As such, the test does not require conformance to any formal performance specifications, and the analyzers neither "officially pass" nor "officially fail" the comparisons. The Phase II test results and other data are presented in Section 3 as a series of figures for each analyzer. The figures in each analyzer's series (Figures 2 through 6, for example) are discussed in their order of appearance. The first (Figure 2) is a typical multipoint calibration curve for the analyzer, showing five or more points spaced over the full-scale range. The span is normally adjusted to a slope of ~2.0 (scale percent/ppm) for a 0-to-50-ppm range. The actual zero (intercept, A) and span (slope, M) shown on the curves are calculated by least squares regression from the actual calibration response data. The sample correlation coefficient provides an empirical measure of the linear association between the analyzer response and the calibration concentrations.

The chronological records of the zero and span drift for each analyzer are shown next in the series of figures (Figure 3). Zero drift is plotted in absolute units (ppm) and the span drift is plotted as the percent difference in the span slope from the nominal slope (not percent-of-scale change in an arbitrary span concentration). Both zero and span drifts are total accumulated drifts except where manual adjustments are explicitly indicated by diamonds situated on the x-axis. The drifts are referenced to the nominal intercept (0 percent of scale) and nominal slope (2.0) represented by the horizontal, dashed lines. Also shown are the nominal adjustment limits for zero (±3 percent of full scale or 1.5 ppm) and span (±7 percent). All adjustment, whether made because nominal drift limits were exceeded or during routine calibrations, are indicated by the diamonds. It is often not possible to adjust the zero and span to the exact nominal values desired because of the nature of the controls. The drift plots are intended mainly for visual comparison among the various analyzers.

The statistics shown above each chart give (1) the total net drift over the entire test period, ignoring adjustments and resets; (2) the number of individual drift periods--i.e., periods between zero and span checks; (3) the average length of the drift periods in days; (4) the average absolute value of the drift for each period (i.e., ignoring the signs of the drifts); and (5) the standard deviation of the individual drifts over all drift periods. The marker at the right side of each chart illustrates a drift range of ±3 standard deviations.

The next figure (Figure 4, for example) is a scatter diagram comparing each subject analyzer measurement (corrected for zero and span drift) with the average of the corresponding measurements from the other analyzers during simultaneous, continuous monitoring of ambient air over approximately 133 days. The linear regression relationship estimated from the data (solid line) is shown along with a dashed line representing the ideal linear relationship (slope = 1, intercept = 0). The linear regression slope and intercept have been tested statistically to determine whether they are significantly different from 1 and 0, respectively. In general, the regression slopes and intercepts are significant even though they approximate the ideal values because of the large number of points (N) used in the regression. Also shown is the sample correlation coefficient (r). The additional dashed lines on the scatter diagram show statistical bounds that should include 90 percent of future analyzer measurements (Y) for any concentration (X) as measured by the average of the reference analyzers. This is a 95-percent confidence interval, based on the estimated linear regression and centered on the estimated regression line, applicable to 90 percent of future observations.* Densely packed data near the origin depict monitoring of unaltered ambient air. The three groups of densely packed data along the curve represent monitoring at three different pollutant augmentation levels of the ambient air.

The next several figures (Figures 5 and 6, for example) present other comparisons of the differences in hourly ambient air readings between subject analyzers and the average of simultaneous readings from other analyzers. Corrections for zero and span drifts are made before the data are compared. The comparison is shown in the form of a frequency distribution indicating numerically and graphically the frequency (number of hours out of the total test period) of the occurrence of each discrepancy versus its magnitude and sign. Also given are the correlation coefficient, the average of the differences (mean difference), the standard deviation of the differences (spread), and the number of absolute differences >2.0 ppm; all of these statistics are calculated with respect to the differences between the hourly readings of the subject analyzer and the average of the corresponding hourly readings from the other analyzers in the test group.

Additional figures show the same type of frequency distribution discussed above but without periodic zero and span corrections; all hourly averages for the subject analyzers are based on the original calibration curve. The reference data from the analyzers on which the comparison is based are still corrected for zero and span drift. Comparison of the data in corresponding sets of frequency distributions, particularly the mean difference and the standard deviation of the differences, illustrates the effect of making periodic zero and span corrections to ambient monitoring data. Usually, the agreement of the hourly readings (bias, spread, or both) is improved by the periodic zero and span adjustments, and the practice is generally recommended where possible.

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*See Lieberman, G. J., and R. G. Miller, Simultaneous tolerance intervals in regression, Biometrika, 50:155-168, 1963, for a more detailed description.

SECTION 3

TEST RESULTS AND DATA FOR DESIGNATED CARBON MONOXIDE ANALYZERS

This section contains summary information on Phase I, and, where available, Phase II postdesignation tests performed on eight carbon monoxide analyzers. Predesignation test data are also given for the ninth designated CO analyzer as reported by the instrument manufacturer/developer in the application for designation. This latter analyzer has not undergone any postdesignation testing as of this writing. The analyzers discussed are presented in Table 1.

TABLE 1. CO ANALYZERS TESTED AND TEST DATES

Manufacturer	Model	Serial No.	Phase I tests	Phase II tests
Beckman	866	1000008	Nov. 1977	May - Sept. 1980
Bendix	8501-5CA	54352-63	Jan. 1981	May - Sept. 1980
Dasibi	3003	039	June 1982	Not yet performed
Horiba	APMA 300E/ 300SE	475990209	June 1982	Not yet performed
Horiba	AQM-10	46795027	Jan.-Oct., 1981	May - Sept. 1980
MASS-CO	Model 1	---	Postdesignation testing not anticipated	
Monitor Labs	8310	NOA1188T	Jan. 1981	May - Sept. 1980
MSA	202S	21125	Nov. 1977	May - Sept. 1980
Thermo Electron	48	ACM-13129-134	June 1982	Not yet performed

TEST RESULTS

Tables 3 through 11 summarize the available Phase I laboratory performance test results for each analyzer and compare these data with EPA specifications and the manufacturer's predesignation test results. Phase II test results for each tested analyzer are shown in a series of figures contained in each analyzer subsection. See Section 2 for an explanation of the tests and figures.

Determination of Minimum Detection Limit (MDL)

Of particular interest for any air monitoring analyzer is its minimum measurement capability. As an aid in determining the lower sensitivity limit of each analyzer, a confidence interval was constructed around zero, using the unbiased estimate of the residuals' variance of a multivariate model. This approach defines the minimum detection limit at a point where an analyzer can distinguish a finite amount of CO from zero. This interval will contain the true value, defined as zero in this case, 90 percent of the time for all future observations.

The statistical approach used assumes that each analyzer measurement is a measure of the true amount of CO in the ambient air at a given time. Using principal components analysis,* a multivariate model can be constructed that predicts a measurement from the estimated true CO concentration. Estimates of the minimum detection limit for the five analyzers subjected to Phase II testing were made using this approach. They are presented in Table 2.

TABLE 2. ESTIMATES OF MINIMUM DETECTION LIMITS

Analyzer	MDL (ppm)
Beckman 866	0.53
Bendix 8501-5CA	0.25
Horiba AQM-10	0.45
Monitor Labs 8310	0.33
MSA	0.61

It should be noted that these estimates of lower sensitivity limits do not include errors associated with other operators and laboratories. Thus, these estimates are probably lower than what would be determined if other variables were included.

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*Lawton, W. H., E. A. Sylvestre, and B. J. Young-Ferraro, Statistical comparison of multiple analytic procedures: Application to clinical chemistry, Technometrics, 21:397-409, 1979.

BECKMAN MODEL 866

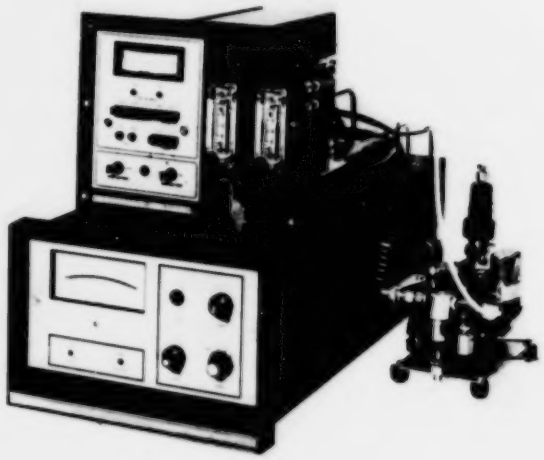


Figure 1. Beckman Model 866 ambient CO monitoring system (RFCA-0876-012). Beckman Instruments, Inc., Process Instruments Division, 2500 Harbor Drive, Fullerton, California 92634.

General Description

The Beckman 866 ambient CO monitoring system operates on the principle of nondispersive infrared spectroscopy described in Appendix A. It is equipped with both a flowing sample cell and a flowing reference cell. Carbon-monoxide-free air is provided for the reference cell by passing a portion of the sample through a catalytic converter that oxidizes CO to CO_2. The analyzer is equipped with dual Luft-type detectors. The combination of the flowing reference cell and narrow bandpass filters for the incident IR radiation minimizes interference from CO_2 and water vapor. An integral Automatic Zero/Span Standardizer allows for automatic zero/span operations on a daily basis.

To be operated as a reference analyzer, the Model 866 must include the following modules:

- Pump/Sample-Handling Module
- Gas Control Panel
- Model 865-17 Analyzer Unit
- Automatic Zero/Span Standardizer.

The analyzer must be operated on the 0-to-50-ppm range with a 13-second electronic response time. Use of the inlet particulate filter is required. Ambient temperature surrounding the analyzer must be in the range of 20° to 30° C; the line voltage to the analyzer must be in the range of 105 to 125 Vac. The analyzer may be operated with or without any of the following options:

- Current output feature
- Linearizer circuit
- Bench mounting kit.

TABLE 3. BECKMAN 866 LABORATORY PERFORMANCE TEST RESULTS

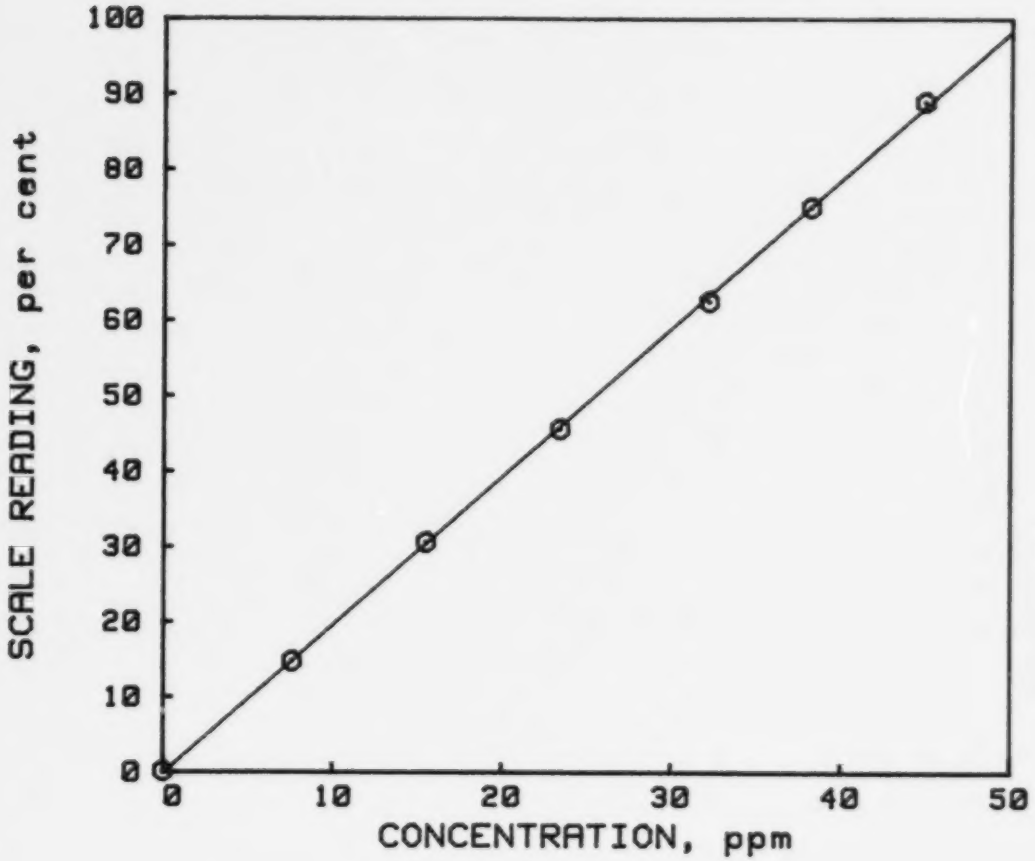
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.50	0.06	0.037
Noise – 80% URL	ppm	0.50	0.08	0.059
Lower detectable limit	ppm	1.0	1.00	1.00
Interferents	ppm			
CO_2		±1.0	0.19	0.10
H_2O		±1.0	0.40	-0.14
Total interferents		±1.5	0.59[d]	0.24[d]
Zero drift – 12 hr	ppm	±1.0	0.53	0.62
Zero drift – 24 hr	ppm	±1.0	0.13[d]	0.08[d]
Span drift – 20% URL	%	±10.0	1.76[d]	1.33[d]
Span drift – 80% URL	%	±2.5	0.16[d]	0.87[d]
Lag time	min	10	0.3	0.2
Rise time	min	5	0.8	0.3
Fall time	min	5	0.7	0.6
Precision – 20% URL	ppm	0.5	0.043	0.067
Precision – 80% URL	ppm	0.5	0.014	0.059

[a]From EPA equivalency regulations, 40 CFR Part 53.

[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests, serial number 1000008.

[d]Average of absolute values.



ANALYZER:	BECKMAN
MODEL:	866
SERIAL No.:	1000008
POLLUTANT:	CO
RANGE:	50 ppm
LOCATION:	DAMDF
DATE:	10/02/80
DATE CODE:	80.276
NAME:	PHASE II

Y = MX + A

M = 1.970
95% C.I.= ± .033

A = -.154
95% C.I.= ± .915

r = .99989

DATA:	X	Y
1	0.000	.100
2	7.600	14.800
3	15.500	30.600
4	23.400	45.600
5	32.200	62.500
6	38.200	75.000
7	44.900	89.000

Figure 2. Typical calibration curve for Beckman 866.

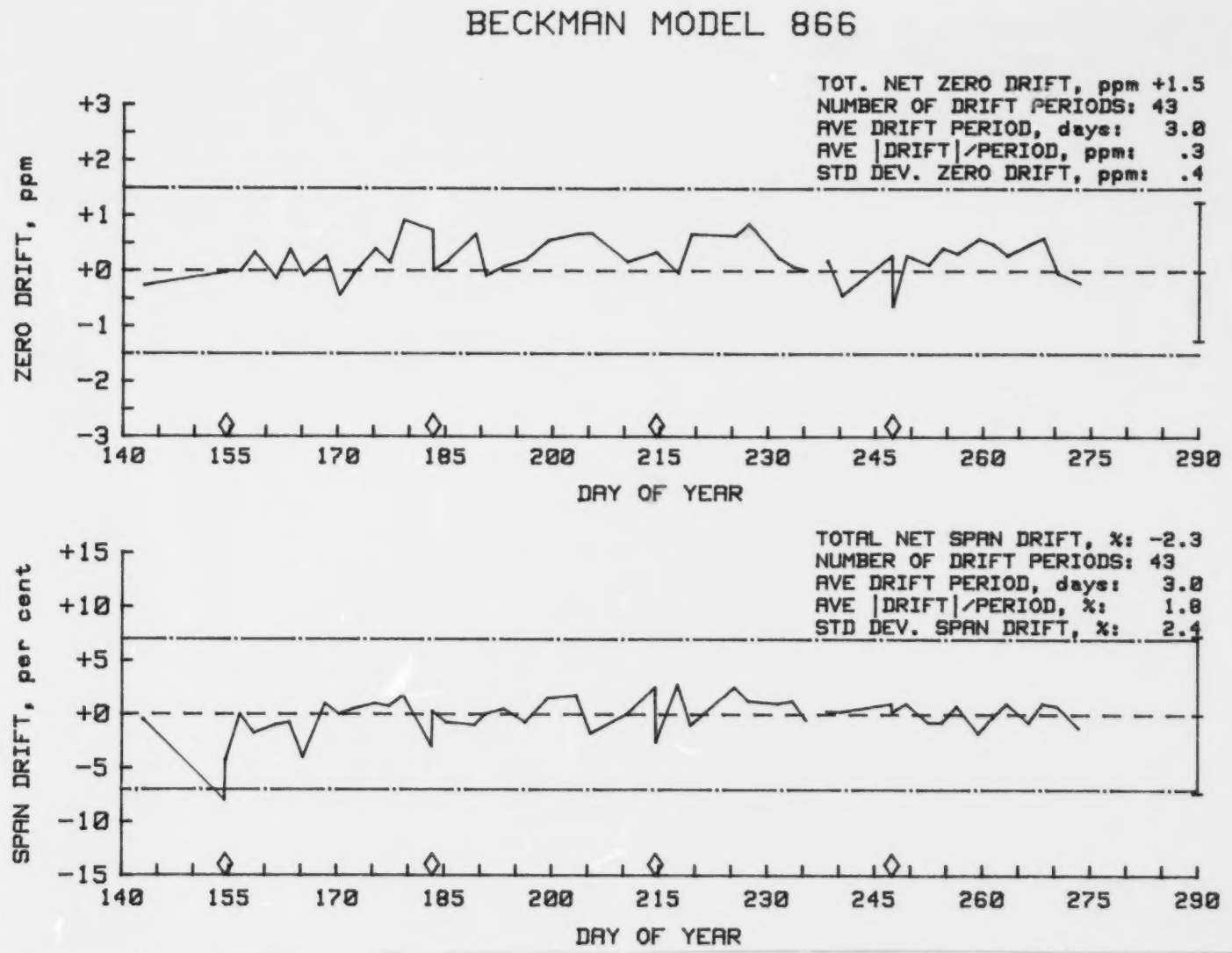


Figure 3. Zero and span drift for Beckman analyzer during Phase II testing.

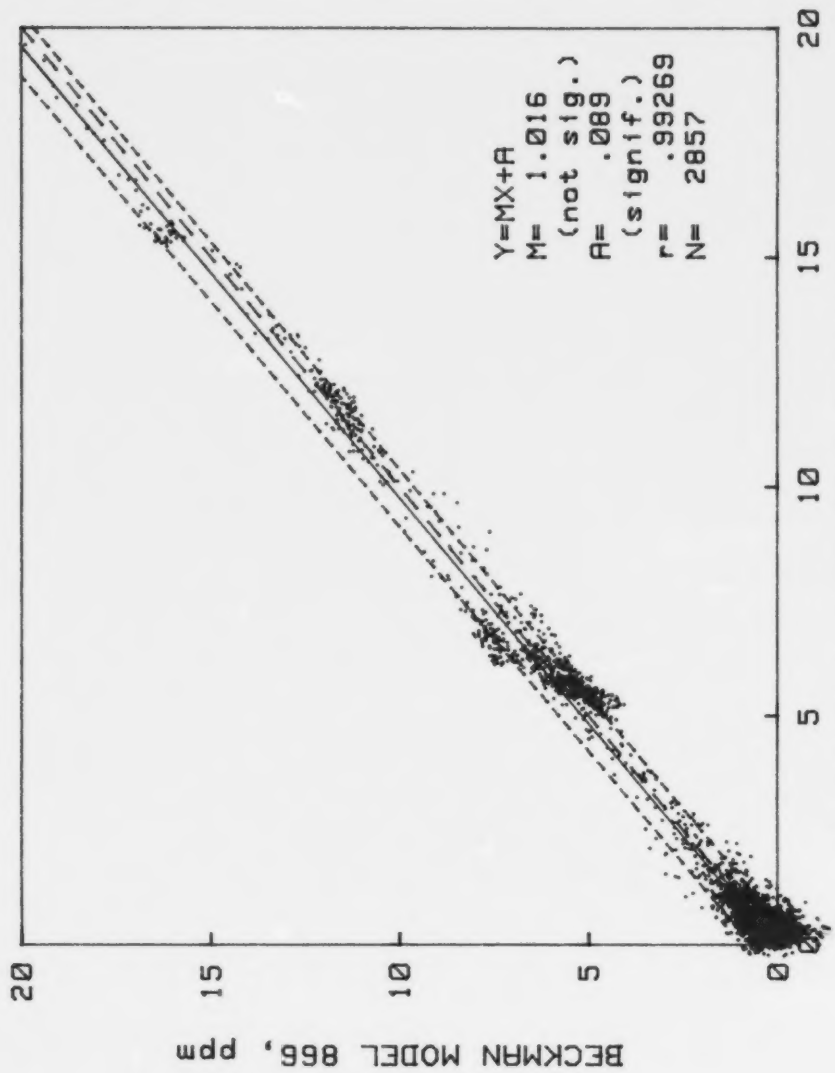


Figure 4. Correlation between the Beckman and the average of the other analyzers during the Phase II ambient monitoring test.

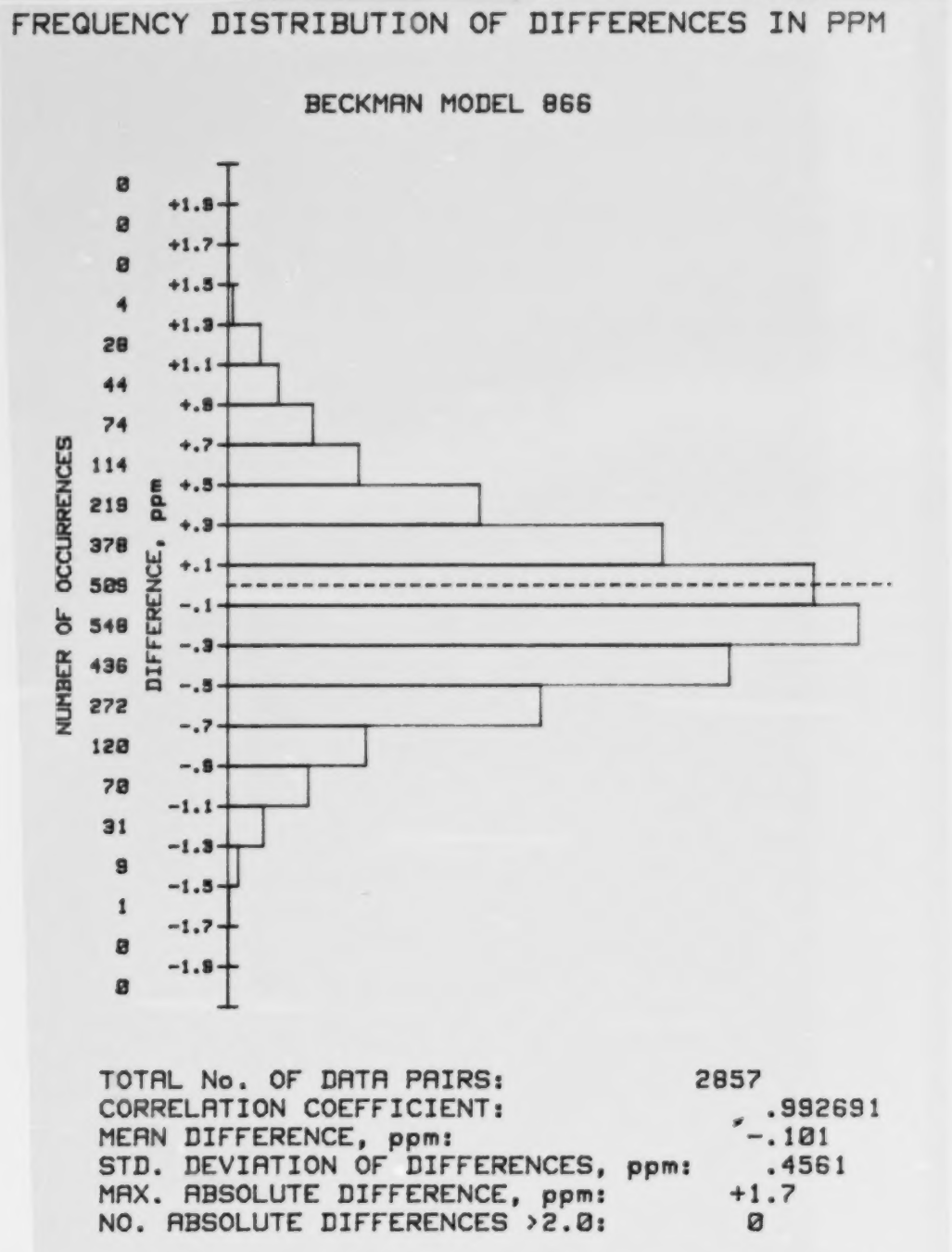


Figure 5. Distribution of differences between the Beckman and the average of the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

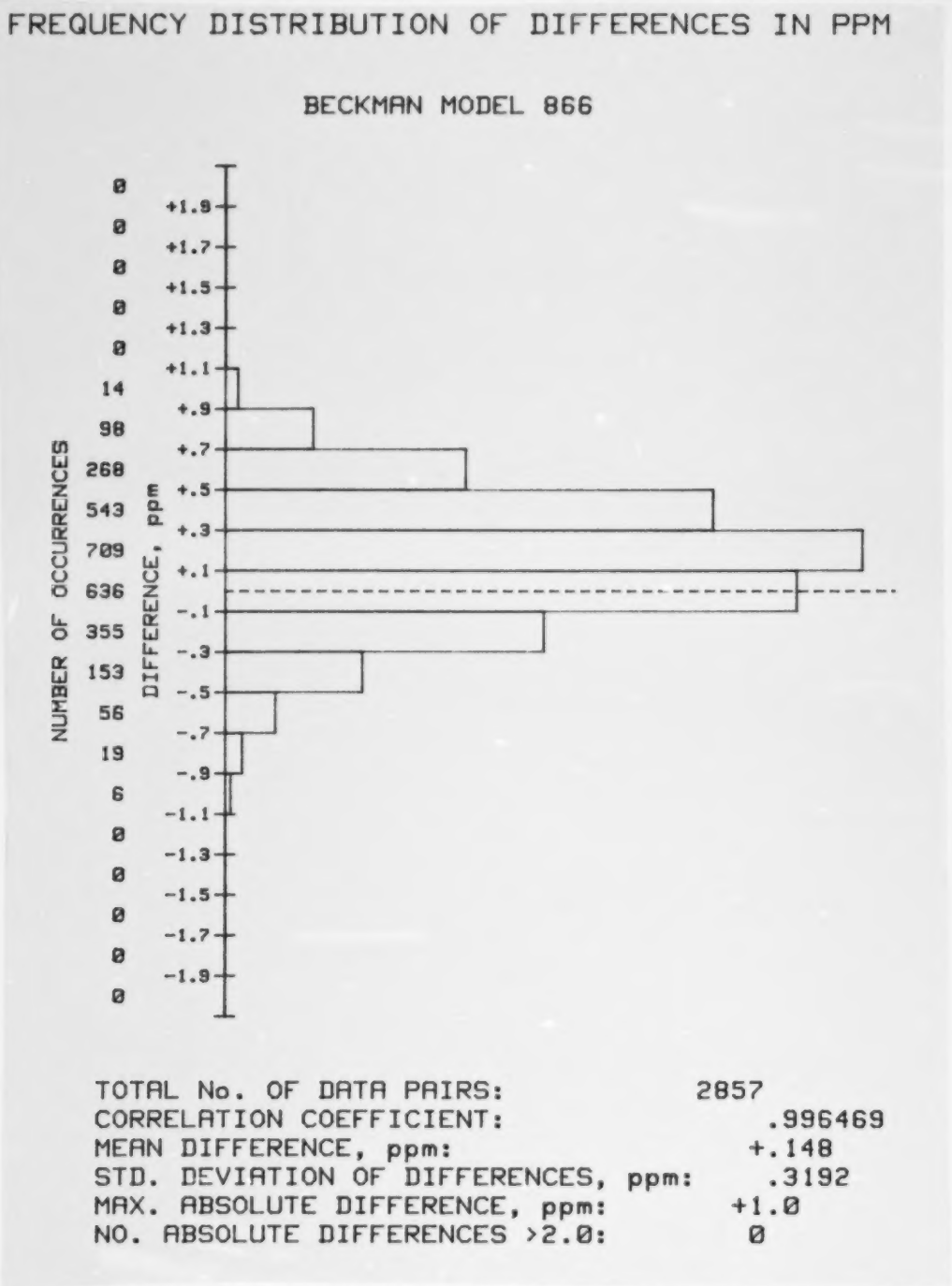


Figure 6. Distribution of differences between the Beckman and the average of the other analyzers during the Phase II ambient monitoring test. Beckman readings not manually corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Log setting of zero control.	Weekly.
Log setting of gain control.	Weekly.
Log sample and reference flowmeter settings.	Weekly.
Check meter reading in TUNE mode.	Weekly.
Check inlet filter F1.	Every 3 weeks.
Check filter/water trap F2.	Every 3 weeks.
Check span gas solenoid.	Every 3 weeks.
Check electronic bias adjustment.	At 1 and 12 weeks.
Check source balance adjustment.	At 1 and 12 weeks.
Check sample and reference filters.	Every 12 weeks.
Check efficiency of catalytic converter.	Every 12 weeks.
Check cell windows.	Semiannually.

Malfunctions

Prior to Phase I testing, faulty infrared sources caused zero baseline drifting. Beckman service personnel replaced the sources and cleaned the cells.

General Comments

Phase I testing was performed on this analyzer immediately after it was received from Beckman in March 1977.

During Phase II testing, the Automatic Zero/Span Standardizer was programmed to perform zero operations every 4 hours and zero/span operations once daily at midnight.

According to the operating manual, the condition of the catalytic converter should be evaluated at 3-month intervals. During Phase II testing, it was discovered that differences in gas humidity between the sample and span inlets influence the results of this evaluation in a way totally unrelated to the condition of the converter.

The evaluation of the converter is accomplished by supplying span gas (80 percent URL) to the span inlet and noting the analyzer's response. The same span gas is then switched to the analyzer's sample inlet and the response is again noted. The two responses are compared and must be within 1 percent full scale of each other for the converter condition to be deemed satisfactory. When span gas is supplied to the span inlet, that gas is supplied directly to the sample cell and whatever gas is present at the sample inlet is supplied, through the converter, to the reference cell.

With the span gas supplied to the sample inlet and the analyzer in the sample mode, span gas is supplied to both the sample and reference cells, although the gas reaching the reference cell has passed through the converter first. If the converter is operating properly, no CO should reach the reference cell. If this condition is true, then the analyzer's response to both inlet configurations will be equal. If, however, the converter is not capable of removing all the CO in the span matrix, then the response to the span gas introduced through the sample inlet will be lower than the response to that introduced through the span inlet.

Span gas is usually a "dry" matrix (i.e., the dewpoint is less than -20° C). When "dry" span gas is supplied to the span inlet and "wet" ambient or room air is supplied to the sample inlet, a humidity difference exists between the sample and reference cells. This difference induces a depression in the analyzer's response that is not induced when dry span gas is present in both cells. Thus, if the converter is close to 100 percent efficient at removing CO, the evaluation will yield an efficiency that seems to be >100 percent. Actual test results yielded an apparent efficiency of 105 percent. Such an enhanced efficiency could lead to a situation in which a converter that is only 95 percent efficient in CO removal (an unacceptable condition) appears to be 100 percent efficient.

It is important to note that this situation can be avoided by supplying dry zero-grade air to the sample inlet while supplying span gas to the span inlet during the first half of the evaluation. The dry matrix should be supplied to the sample inlet for approximately 30 minutes to ensure that the converter is in a "dry" condition before any converter test data are accepted from the analyzer. This procedure will ensure that the sample/reference humidity ratio is unity throughout the evaluation. This, in turn, will ensure that the evaluation reflects the true ability of the converter to oxidize CO.

The data presented in Figures 5 and 6 seem to indicate a slightly better performance by the analyzer when corrections for long-term zero and span drift were not applied. This observation was surprising since such corrections usually enhance the quality of the data considerably. After further consideration of the data, the analyzer, and the test conditions, the following mechanism was advanced to explain this phenomenon.

This instrument was operated throughout the Phase II test with automatic zero correction every 4 hours and automatic span correction every 24 hours. Additionally, manual zero and span corrections, updated every 2 to 3 days, were applied to the data. When a drift from nominal performance was detected by the manual zero/span check, it was corrected for immediately by modifying the current calibration curve used to scale the test data base. Approximately 12 hours after such a correction, the instrument itself reacted (through its automatic zero/span procedure) to reestablish nominal performance. However, the corrections to the data base continued to be applied until the next manual zero/span check, which would, most probably, set up a similar set of conditions for the next 2- to 3-day period. Thus, the

manual and automatic zero/span procedures worked against each other producing data that were inferior to those produced by the automatic procedure alone (reported as data unadjusted for manual zero/span operations in Figure 6).

It is recommended, therefore, that users of analyzers employing or requiring automatic zero/span operations evaluate the effect of manual zero/span operations on their data quality. It may be advisable to use a manual zero/span check only, in such cases, and depend on the analyzer's automatic operation for routine zero and span drift corrections. Under such conditions, however, it would be absolutely necessary to maintain tight control on the quality of the zero and span standards used for the automatic operation.

Phase III testing: In the fall of 1977, EPA Region 4 asked MSB to investigate a problem that existed with the designated Beckman 866 CO analyzers in the Charlotte, North Carolina, monitoring program. The problem was described as a nonlinearity at the low end of the calibration curve that was not consistent from calibration to calibration. After investigation of the problem both in the EPA laboratories at RTP and the Charlotte monitoring sites, the problem was determined to be due to retention of moisture in the CO converter in the reference cell path of the analyzer. When dry zero or calibration gas was introduced into the analyzer following normal ambient monitoring, the CO converter released moisture into the reference cell for some period of time, causing the gas in the reference cell to have a higher humidity than that in the sample cell. The unequal humidities in the two cells caused the analyzer reading to be depressed by about 1 ppm. This transient upset condition lasted from about 10 minutes in the EPA analyzer at the RTP laboratory to over 1 hour in some of the analyzers at the Charlotte sites, after which time the analyzer reading returned to normal.

Because the moisture content in ambient air changes very slowly, no adverse effects would occur during ambient monitoring. However, special calibration and zero/span procedures were found to be necessary to avoid a calibration error from this effect. Working with EPA, Beckman Instruments prepared an addendum to the calibration procedure prescribed in the original analyzer instruction manual and distributed it to all purchasers of the designated model. The addendum is now included in the instruction manual furnished with new analyzers.

BENDIX MODEL 8501-5CA

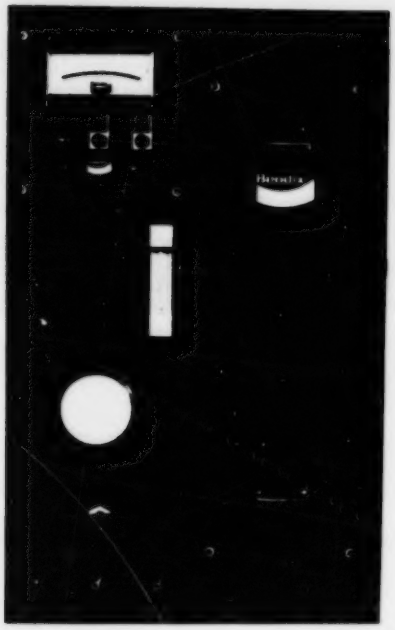


Figure 7. Bendix Model 8501-5CA infrared CO analyzer (RFCA-0276-008). Bendix Corporation, Environmental and Process Instruments Division, P.O. Box 831, Lewisburg, West Virginia 24901.

General Description

The Bendix Model 8501-5CA infrared CO analyzer operates on the principle of nondispersive infrared spectroscopy described in Appendix A. It is equipped with a flowing sample cell and a sealed, nitrogen-containing reference cell. The detector is of the Luft type, but double chambers are provided within the detector to compensate for minor CO_2 and water vapor interference.

To be used as a reference analyzer, the 8501-5CA must be operated on the 0-to-50-ppm range with a time constant setting between 5 and 16 seconds. Use of the inlet sample filter is required. The ambient temperature surrounding the analyzer must be in the range of 20° to 30° C; the line voltage to the analyzer must be in the range of 105 to 125 Vac. The analyzer may be used with or without the following options:

- Rack mounting with chassis slides
- Rack mounting without chassis slides
- External sample pump.

TABLE 4. BENDIX 8501-5CA LABORATORY PERFORMANCE TEST RESULTS

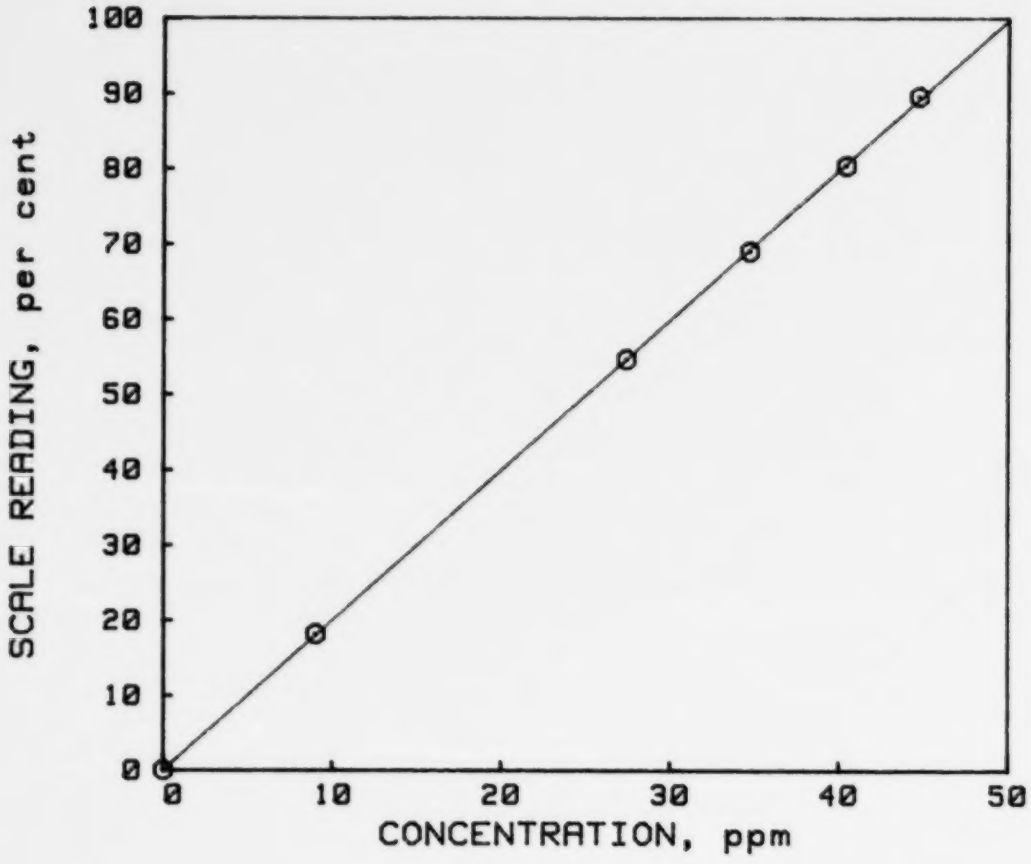
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.50	0.050	0.042
Noise – 80% URL	ppm	0.50	0.059	0.073
Lower detectable limit	ppm	1.0	1.00	1.03
Interferents	ppm			
CO_2		±1.0	0.20	0.00
H_2O		±1.0	0.15	0.22
Total interferents		±1.5	0.35[d]	0.24[d]
Zero drift – 12 hr	ppm	±1.0	0.26	0.41
Zero drift – 24 hr	ppm	±1.0	0.23[d]	0.40[d]
Span drift – 20% URL	%	±10.0	2.46[d]	2.79[d]
Span drift – 80% URL	%	±2.5	0.47[d]	0.38[d]
Lag time	min	10	1.0	0.5
Rise time	min	5	1.8	1.0
Fall time	min	5	1.7	0.8
Precision – 20% URL	ppm	0.5	0.034	0.032
Precision – 80% URL	ppm	0.5	0.035	0.108

[a]From EPA equivalency regulations, 40 CFR Part 53.

[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests, serial number 54351-90.

[d]Average of absolute values.



ANALYZER:	BENDIX
MODEL:	8501-5CA
SERIAL No.:	54351-90
POLLUTANT:	CO
RANGE:	50 ppm
LOCATION:	DAMDF
DATE:	07/01/80
DATE CODE:	80.183
NAME:	PHASE II

Y = MX + A

M = 1.994
95% C.I.= ± .020

A = .064
95% C.I.= ± .601

r = .99998

DATA:	X	Y
1	0.000	0.000
2	9.000	18.200
3	27.400	54.700
4	34.700	69.000
5	40.400	80.400
6	44.700	89.600

Figure 8. Typical calibration curve for Bendix 8501-5CA.

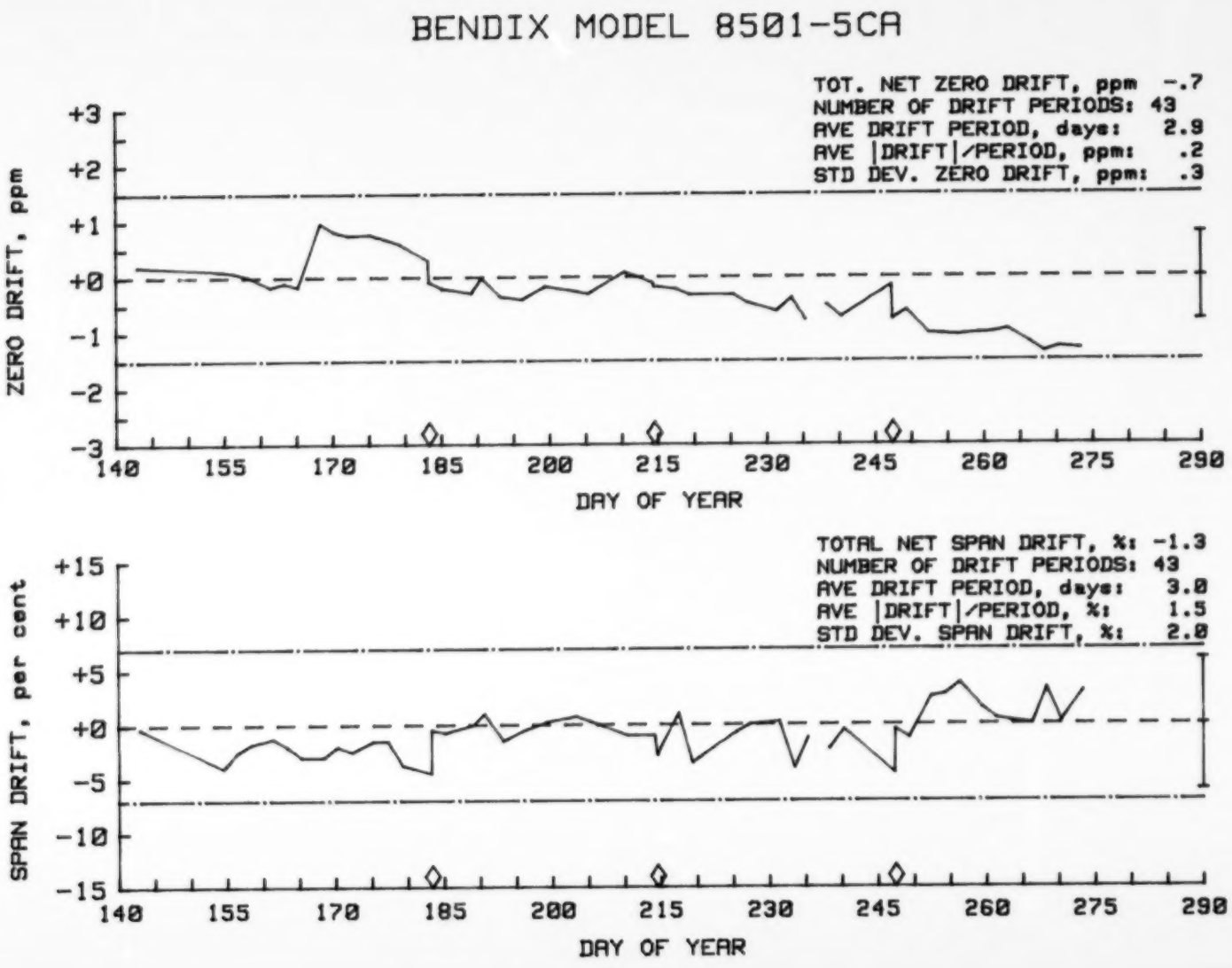


Figure 9. Zero and span drift for Bendix analyzer during Phase II testing.

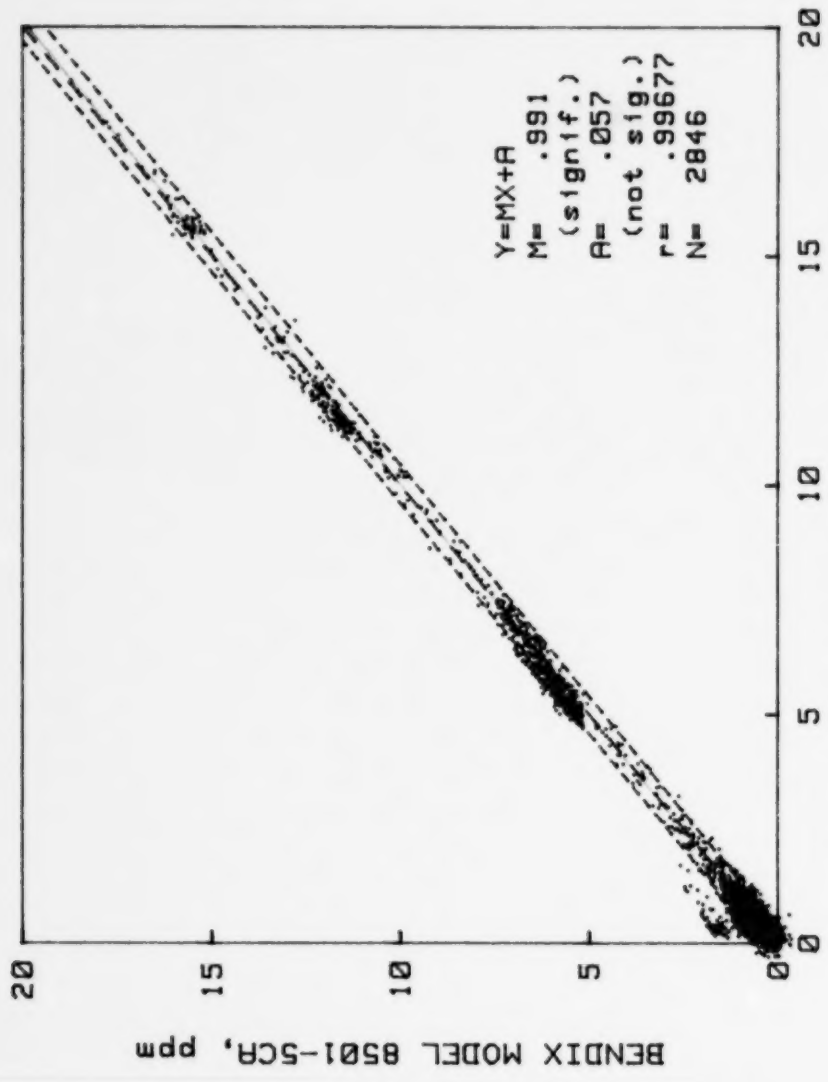


Figure 10. Correlation between the Bendix and the average of the other analyzers during the Phase II ambient monitoring test.

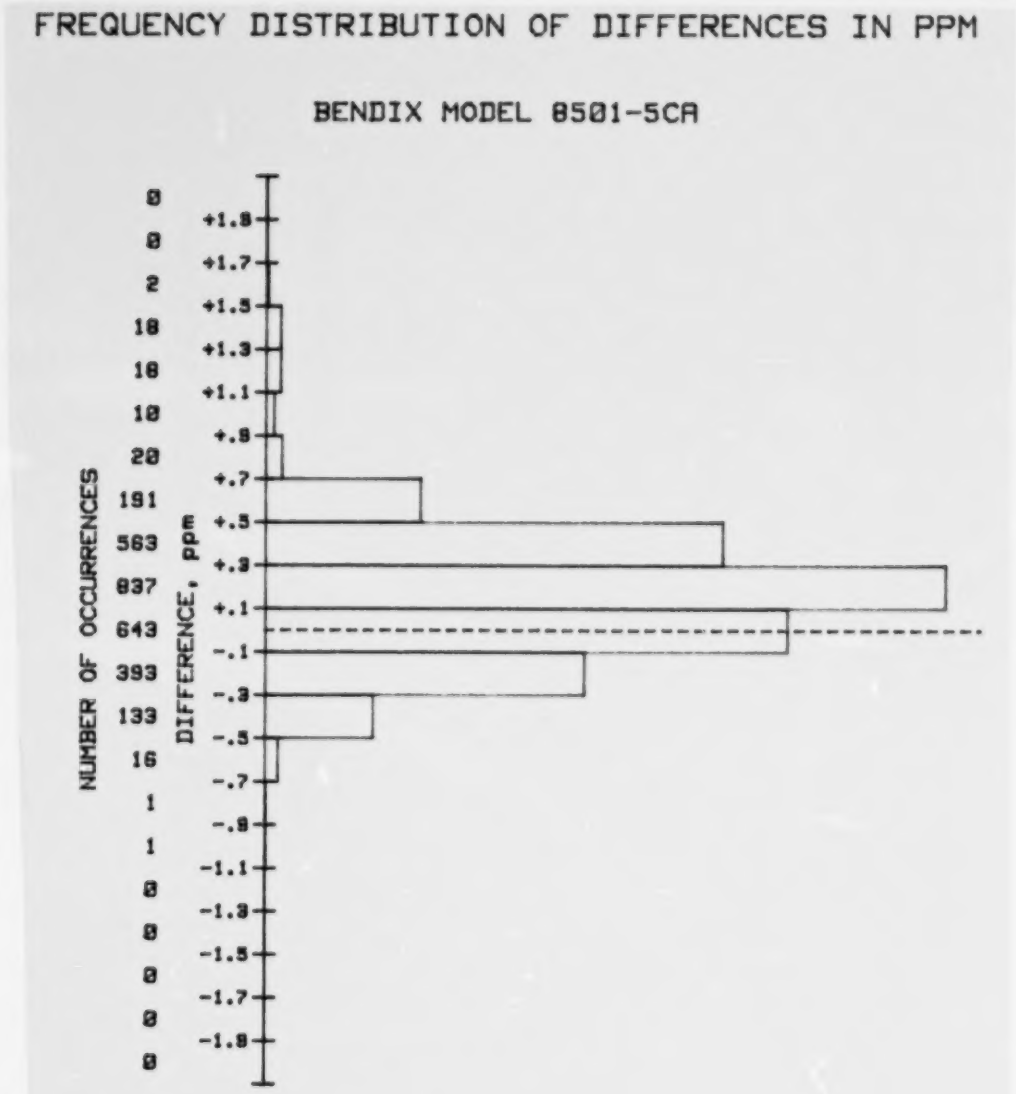


Figure 11. Distribution of differences between the Bendix and the average of the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

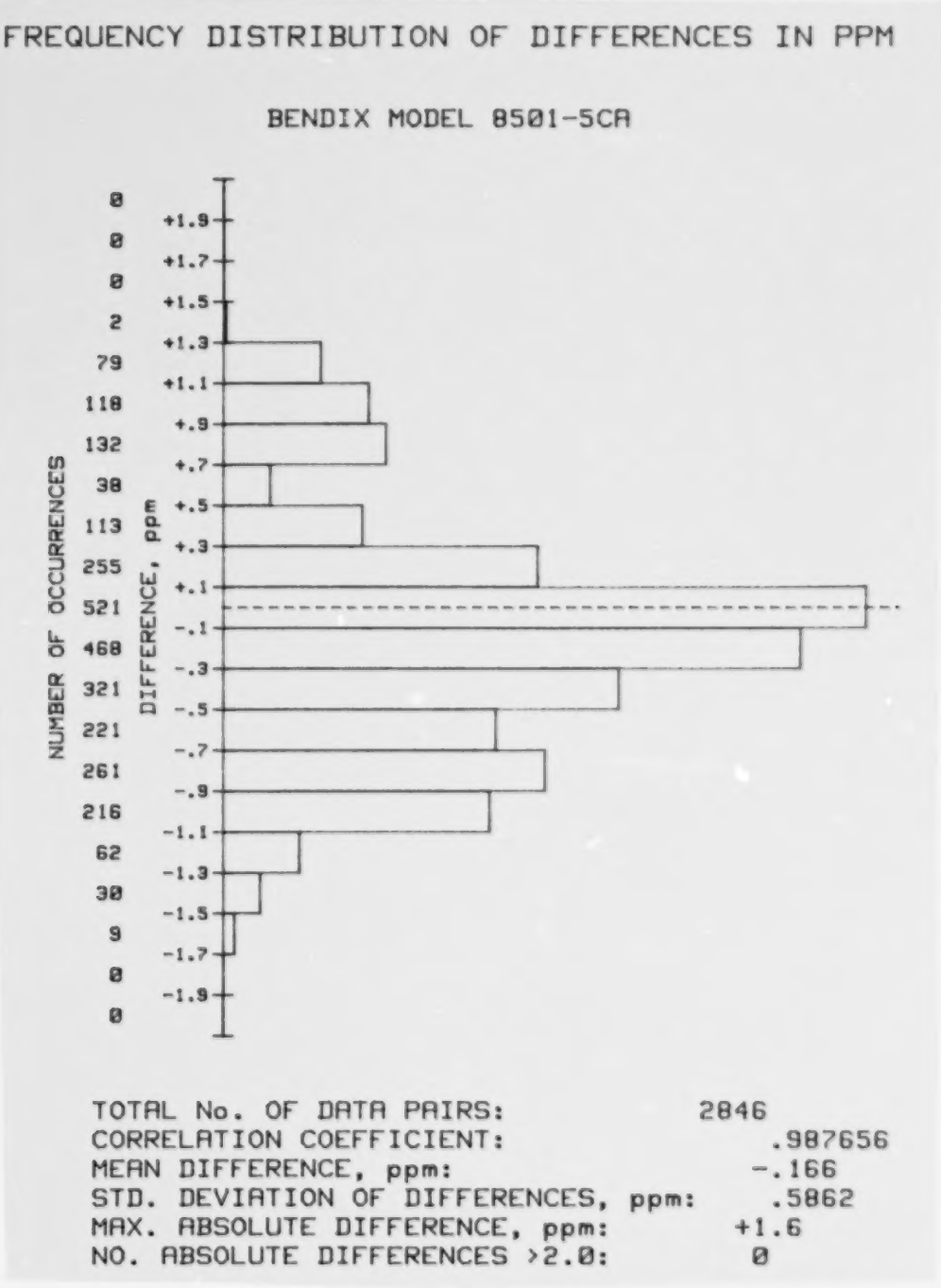


Figure 12. Distribution of differences between the Bendix and the average of the other analyzers during the Phase II ambient monitoring test. Bendix readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Check input sample filter (8 μm).	Weekly.
Replace input sample filter (8 μm).	Monthly.
Check gas filter.	Monthly.
Replace gas filter.	Semiannually.
Sample pump maintenance.	As required.
Clean interior and exterior of instrument.	As required.

Malfunctions

No malfunctions were experienced throughout Phase I or Phase II testing.

General Comments

Prior to postdesignation equivalency testing, this analyzer had been operated routinely as an ambient air CO monitor at the EPA DAMDF for ~18 months. Before the testing began, a representative of the manufacturer examined the instrument and stated that it was in good condition and capable of normal performance.

During the postdesignation testing, the analyzer was operated with a 5-second time constant and the output signal smoothing filter according to the reference designation and to the manufacturer's recommendation.

During Phase II testing, the zero/span check routine followed the sequence:

1. Transfer analyzer inlet from ambient air to span matrix.
2. Measure unadjusted span response.
3. Transfer analyzer inlet from span matrix to zero matrix.
4. Measure unadjusted zero response.
5. Adjust zero response (if necessary).
6. Measure adjusted zero response (if necessary).
7. Transfer analyzer inlet from zero matrix to span matrix.
8. Adjust span response (if necessary).
9. Measure adjusted span response (if necessary).
10. Transfer analyzer inlet from span matrix to ambient air.

During this sequence, the analyzer response to the first span matrix often seemed to stabilize at a level 1½ to 2 percent (~1 ppm) below the final value, drifting to the final value over the next 45 to 60 minutes. However, during response to the second span matrix (where the analyzer

sample inlet was transferred from the zero matrix to the span matrix), equilibrium was established at the final value within 2 or 3 minutes of span introduction. It is believed that this behavior can be attributed to desorption of water vapor from the analyzer's paper sample filters during the first 45 minutes of initial dry span matrix introduction. The water vapor was originally deposited in the filters during ambient sampling because of the ambient humidity present in the sample matrix. The gradual desorption of the water vapor caused a decreasing humidity within the sample cell, which, in turn, caused the drifting of the output signal. The same behavior was not noted during the second span period, probably because the analyzer had been sampling a dry matrix for 1 to 1½ hours prior to second span introduction. This effect was observed over a range of ambient humidities (56 to 96 percent relative humidity). The magnitude of the effect did not seem to depend on the level of humidity in the sample matrix.

During Phase I testing, routine water vapor interferent tests were conducted with carbon monoxide levels at 10 ppm ± 10 percent and water vapor levels at 20,000 ppm ± 10 percent. The drifting effect was not observed. Additional testing of this phenomenon has been performed at the 20-percent-of-scale level (10 ppm CO). During these tests, the drifting behavior was observed in some cases and not observed in others. When it was observed, its magnitude was less than the 1½ to 2 percent observed at the 90-percent-of-scale level. It is currently believed that the magnitude of this phenomenon is roughly proportional to the concentration at which it is observed. The maximum effect (~1 ppm) occurs at the upper end of the analysis scale and is usually observed during routine span operations. It is also believed that the phenomenon does not represent a significant degradation in routine monitoring data quality. It is recommended only that users of this analyzer be aware of the existence of the phenomenon. Its effect may be negated entirely, if desired, by allowing sufficient time (e.g., 1 hour) to elapse both preceding and following calibration with dry gas before data from the analyzer are considered valid.

During Phase I testing, this analyzer's sensitivity to external vibration was noted. Such vibration, ranging from closing the test chamber door to operating water bubblers adjacent to the analyzer on the same table, induced output signal noise levels of 5 to 7 percent of scale. Therefore, it was necessary to employ unusual conditions to eliminate vibration during testing. No entrance into the chamber was permitted for any reason during testing. All sources of vibration were physically separated from the analyzer. However, it must be noted that noise of the magnitude observed during this test would not necessarily cause failure of the equivalency designation noise specification.

During its history, this analyzer has been equipped with two optical bench configurations--the older configuration (colored silver or gray) and the newer configuration (colored gold). The difference between these bench configurations that is of interest to the average user lies in the mechanism employed to obtain a balance in the IR energy transmitted to the sample cell and the reference cell. The old configuration achieved balance by physically moving the IR source with respect to the openings of the two cells. The newer configuration uses a fixed source and employs a mirror and "shading screws" to achieve balance between the cells. The analyzer actually evaluated during this test was equipped with an "old configuration" optical bench.

DASIBI MODEL 3003

Figure 13. Dasibi Model 3003 gas filter correlation CO analyzer (RFCA-0381-051). Dasibi Environmental Corporation, 616 E. Colorado Street, Glendale, California 91205.

General Description

The Dasibi Model 3003 gas filter correlation CO analyzer operates on the principle of gas filter correlation (GFC) NDIR spectroscopy described in Appendix A. It is equipped with a solid-state detector and multiple pass optics in the sample cell. The effects of interfering species on the measurement are minimized by the nature of the GFC technique itself.

To be used as a reference analyzer, the 3003 must be operated on the 0-to-50-ppm range with a sample particulate filter installed in the sample inlet line. Ambient temperature surrounding the analyzer must be in the range of 20° to 30° C; line voltage to the analyzer must be in the range of 105 to 125 Vac. The analyzer may be used with or without any of the following options:

- Rack mount
- Remote zero and span
- BCD digital output
- 4-20 milliamp output.

TABLE 5. DASIBI 3003 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.50	0.051	0.107
Noise – 80% URL	ppm	0.50	0.075	0.158
Lower detectable limit	ppm	1.0	0.81	1.05
Interferents	ppm			
CO_2		±1.0	0.0	-0.42
H_2O		±1.0	-0.1	0.06
Total interferents		±1.5	0.1[d]	0.49[d]
Zero drift–12 h	ppm	±1.0	0.6	–[e]
Zero drift–24 h	ppm	±1.0	0.3[d]	–[e]
Span drift–20% URL	%	±10.0	4.0[d]	–[e]
Span drift–80% URL	%	±2.5	1.4[d]	–[e]
Lag time	min	10	0.1	–[e]
Rise time	min	5	1.1	–[e]
Fall time	min	5	0.8	–[e]
Precision–20% URL	ppm	0.5	0.038	–[e]
Precision–80% URL	ppm	0.5	0.053	–[e]

[a]From EPA equivalency regulations, 40 CFR Part 53.

[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests, serial number 039.

[d]Average of absolute values.

[e]Tests not complete (see general comments section.)

Manufacturer's Recommended Maintenance

Operation	Frequency
Sight, sound, and touch check.	Whenever an operator is present.
Replace sample filter.	Weekly.

Malfunctions

During Phase I testing in June 1982, the analyzer failed 12- and 24-hour zero drift, and 24-hour 20- and 80-percent-of-scale tests; see comment below.

General Comments

During Phase I postdesignation testing, this analyzer failed 20- and 80-percent-of-scale drift tests on Test Day 2. Additionally, 12- and 24-hour zero drift, as well as 20- and 80-percent-of-scale drift tests, were failed on Test Day 3. All drift values were acceptable during Day 1 testing; Day 4 testing was not conducted due to failure of the analyzer's IR source.

As of this writing, the cause of these failures is unknown. The analyzer has been returned to the Dasibi facility in Glendale, California, for service. When the problem is resolved, testing will be repeated. The cause of the failure and the results of the repeated tests will be reported in a future edition of this document.

No Phase II testing has been conducted as of this writing.

HORIBA MODEL APMA 300E/300SE

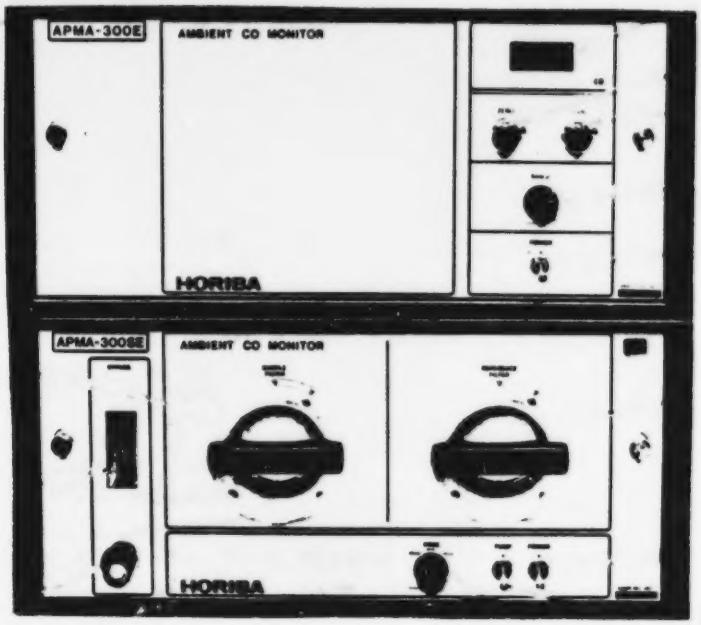


Figure 14. Horiba Model APMA 300E/300SE ambient carbon monoxide monitoring system (RFCA-1180-048). Horiba Instruments, Incorporated, 1021 Duryea Avenue, Irvine Industrial Complex, Irvine, California 92714.

General Description

The Horiba Model APMA 300E/300SE ambient carbon monoxide monitoring system operates on the principle of nondispersive infrared spectroscopy described in Appendix A. An unusual feature of this analyzer, however, is the use of a cross-flow modulation technique rather than the usual mechanical chopper modulation technique. The analyzer is equipped with two flowing cells and is configured so that sample and reference matrices are alternately directed through each cell at a frequency of once per minute. This configuration, along with low volume cells (11 cm^3, 35 mm in length) and high sample demand rates (7-11 L/min), is designed to increase sensitivity and baseline stability.

The analyzer is equipped with dual-chambered detectors of the Luft design, which, in conjunction with optical filters and the cross-flow technique itself, minimize the effect of water vapor and CO_2 interference. The CO-free matrix required as the reference gas is provided within the analyzer by passing a portion of the sample gas through a catalytic oxidizer that converts CO to CO_2.

The analyzer is supplied in two modules. The 300E module is the analyzer itself; the 300SE is the sample handling module containing the valving, pumps, catalytic oxidizer, etc.

To be used as a reference analyzer, the 300E/300SE must be operated on the 0-to-20-ppm range, the 0 to 50 ppm range, or the 0-to-100-ppm range. The time constant switch must be set to position 5 regardless of which range is selected. The analyzer is designated with an extended operating temperature range of 10° to 40° C. The line voltage to the analyzer must be in the range of 105 to 125 Vac.

TABLE 6. HORIBA APMA 300E/300SE LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise–0% URL	ppm	0.50	0.029	0.031
Noise–80% URL	ppm	0.50	0.042	0.061
Lower detectable limit	ppm	1.0	0.58	0.76
Interferents	ppm			
CO_2		±1.0	0.44	-0.04
H_2O		±1.0	0.02	0.08
Total interferents		±1.5	0.47[d]	0.14[d]
Zero drift–12 h	ppm	±1.0	0.22	0.20
Zero drift–24 h	ppm	±1.0	0.02[d]	0.05[d]
Span drift–20% URL	%	±10.0	0.19[d]	0.91[d]
Span drift–80% URL	%	±2.5	0.31[d]	0.70[d]
Lag time	min	10	0.1	<0.2
Rise time	min	5	0.6	0.6
Fall time	min	5	0.6	0.9
Precision–20% URL	ppm	0.5	0.019	0.044
Precision–80% URL	ppm	0.5	0.035	0.035

[a]From EPA equivalency regulations, 40 CFR Part 53.

[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests, serial number 475990209.

[d]Average of absolute values.

Manufacturer's Recommended Maintenance

Operation	Frequency
Check flow rate.	Weekly.
Perform internal zero/span check.	Daily.
Perform external zero/span check.	Biweekly.
Perform filter paper visual check.	Weekly.
Perform compensation check.	Semiannually.
Check catalyst efficiency.	Quarterly.
Establish calibration curve.	Quarterly.
Check inlet port filters.	Annually.
Check sample cell condition.	Annually.
Check motor valve seal.	Annually.

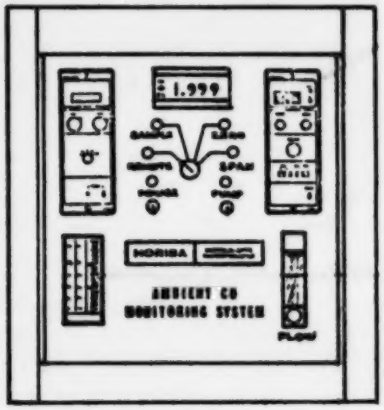
Malfunctions

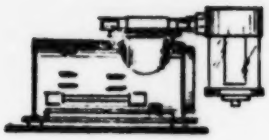
No malfunctions were noted throughout Phase I testing.

General Comments

Phase I testing was conducted during June 1982. Phase Il testing has not been conducted as of this writing.

HORIBA MODELS AQM-10, -11, -12





Sample Pump with Filter

AIA-24 AS Analyzer Section

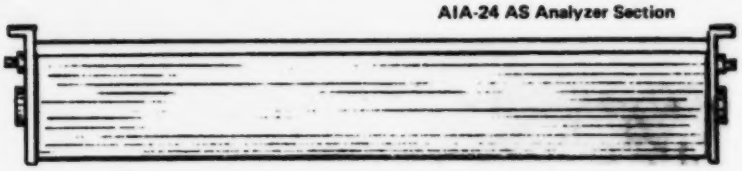


Figure15. Horiba Model AQM-10 ambient CO monitoring system (RFCA-1278-033). Horiba Instruments, Incorporated, 1021 Duryea Avenue, Irvine Industrial Complex, Irvine, California 92714.

General Description

The Horiba AQM-10, -11, and -12 ambient CO monitoring systems operate on the principle of nondispersive infrared spectroscopy described in Appendix A. They are equipped with a flowing sample cell and a sealed, nitrogen-containing reference cell. The dual detectors are of the Luft type, and infrared radiation is provided by dual sources. Interference from sample gas water vapor is minimized by compensation provided by the dual sample and reference chambers within the detector. An option, the AIC-101 Automatic Indication Corrector, allows for automatic zero/span operations on a daily basis.

The AQM-10, -11, and -12 analyzers differ only in the way they are mounted. The AQM-10 is rack-mounted in a customer-provided rack, the AQM-11 is mounted in a table-top cabinet, and the AQM-12 is mounted in a floor-standing cabinet.

To be used as a reference analyzer, the AQM-10, -11, or -12 analyzers must be operated on the 0-to-50-ppm range (range 2) with a response time setting of 15.5 seconds. Ambient temperature surrounding the analyzer must be in the range of 20° to 30° C and the line voltage to the analyzer must be in the range of 105 to 125 Vac. The analyzers may be operated with or without any of the following options:

- AIC-101 automatic indication corrector
- VIT-3 non-isolated current output
- ISO-2 and DCS-3 isolated current output.

TABLE 7. HORIBA AQM-10 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.50	0.046	0.043[e]
Noise – 80% URL	ppm	0.50	0.046	0.098[e]
Lower detectable limit	ppm	1.0	1.01	0.62[e]
Interferents	ppm			
CO_2		±1.0	0.39	0.22[f]
H_2O		±1.0	0.12	0.42[f]
Total interferents		±1.5	0.52[d]	0.65[d,f]
Zero drift – 12 h	ppm	±1.0	0.19	0.20[f]
Zero drift – 24 h	ppm	±1.0	0.11[d]	0.25[d,f]
Span drift – 20% URL	%	±10.0	1.21[d]	1.54[d,f]
Span drift – 80% URL	%	±2.5	0.62[d]	0.67[d,f]
Lag time	min	10	0.2	0.3[e]
Rise time	min	5	0.5	0.2[e]
Fall time	min	5	0.5	0.3[e]
Precision – 20% URL	ppm	0.5	0.054	0.046[f]
Precision – 80% URL	ppm	0.5	0.057	0.040[f]

[a]From EPA equivalency regulations, 40 CFR Part 53.

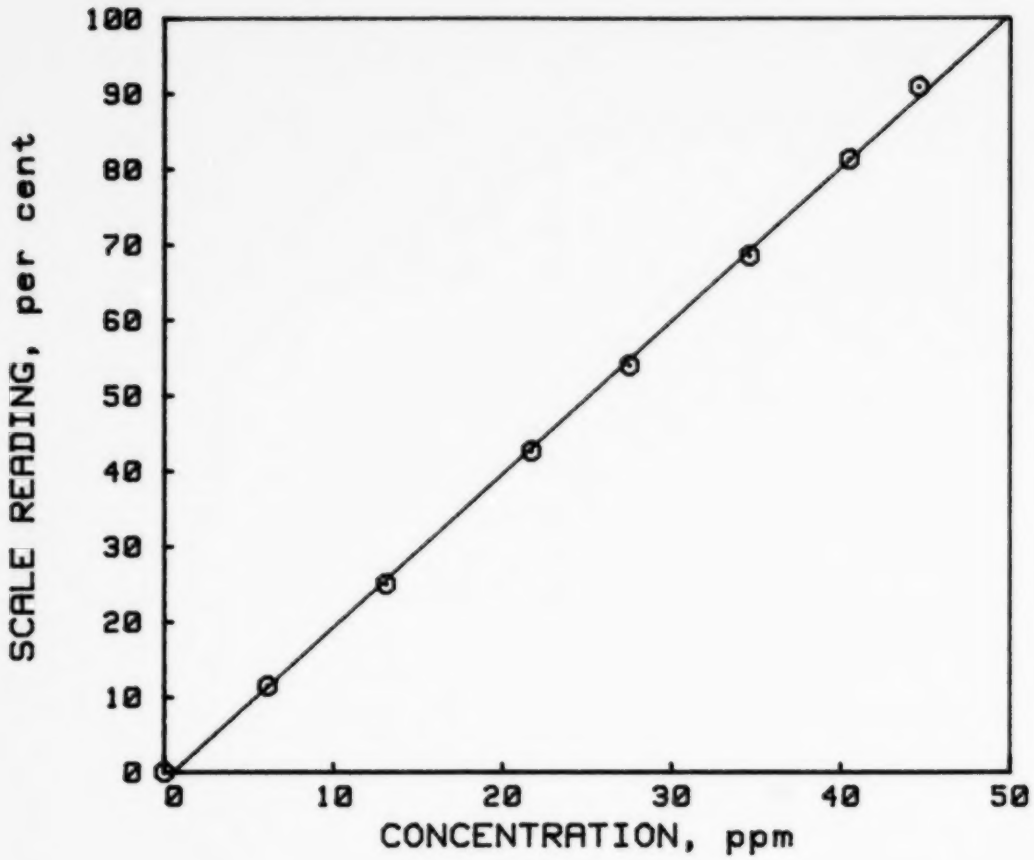
[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests, serial number 46795027.

[d]Average of absolute values.

[e]Average, from original Phase I postdesignation test.

[f]Average, from manufacturer – repeated portions of Phase I postdesignation test (see general comments section).



ANALYZER:	HORIBA
MODEL:	AQM-10
SERIAL No.:	46795027
POLLUTANT:	CO
RANGE:	50 ppm
LOCATION:	DAMDF
DATE:	07/31/80
DATE CODE:	80.213
NAME:	PHASE II

Y = MX + A

M = 2.030

95% C.I.= ± .050

A = -1.014

95% C.I.= ± 1.486

r = .99969

DATA:	X	Y
1	0.000	0.000
2	6.110	11.500
3	13.100	25.000
4	21.700	42.600
5	27.500	54.000
6	34.600	68.500
7	40.500	81.300
8	44.600	90.900

Figure 16. Typical calibration curve for Horiba AQM-10.

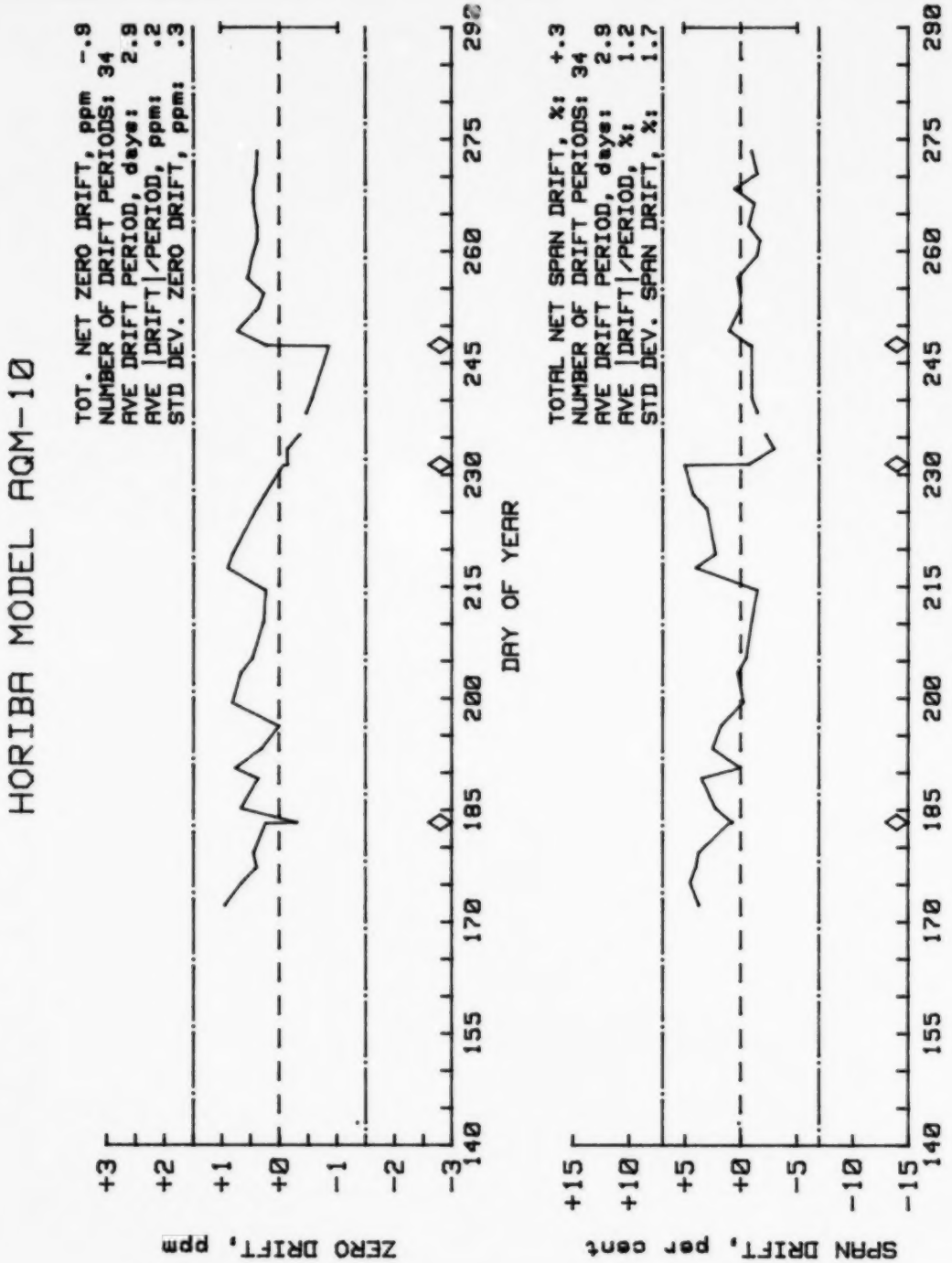


Figure 17. Zero and span drift for Horiba analyzer during Phase II testing.

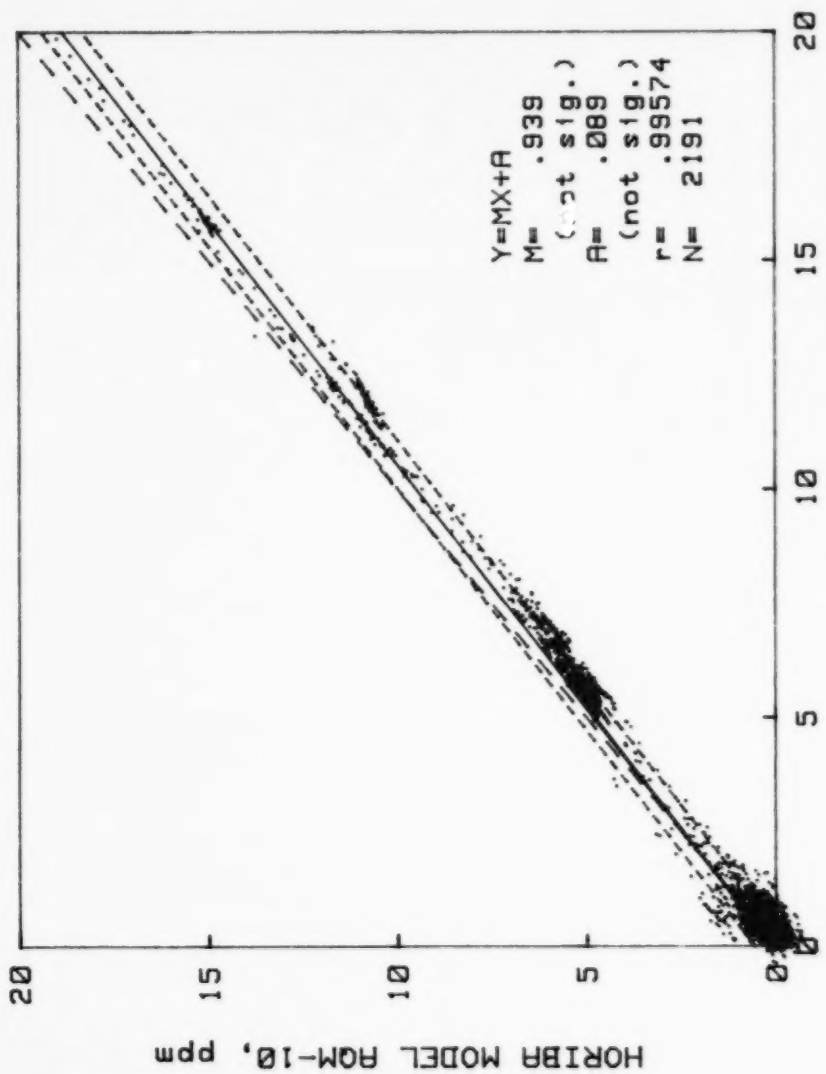


Figure 18. Correlation between the Horiba and the average of the other analyzers during the Phase II ambient monitoring test.

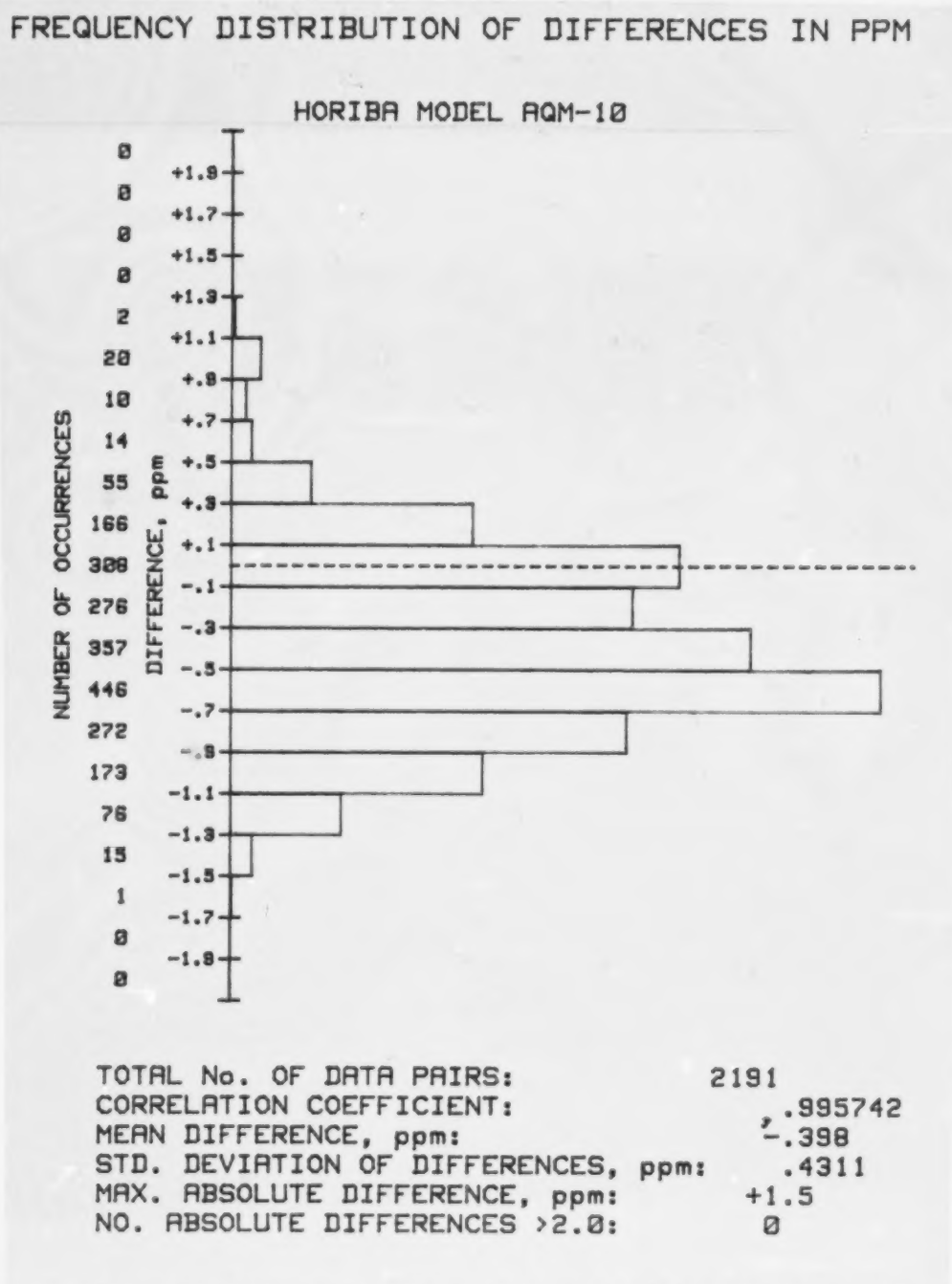


Figure 19. Distribution of differences between the Horiba and the average of the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

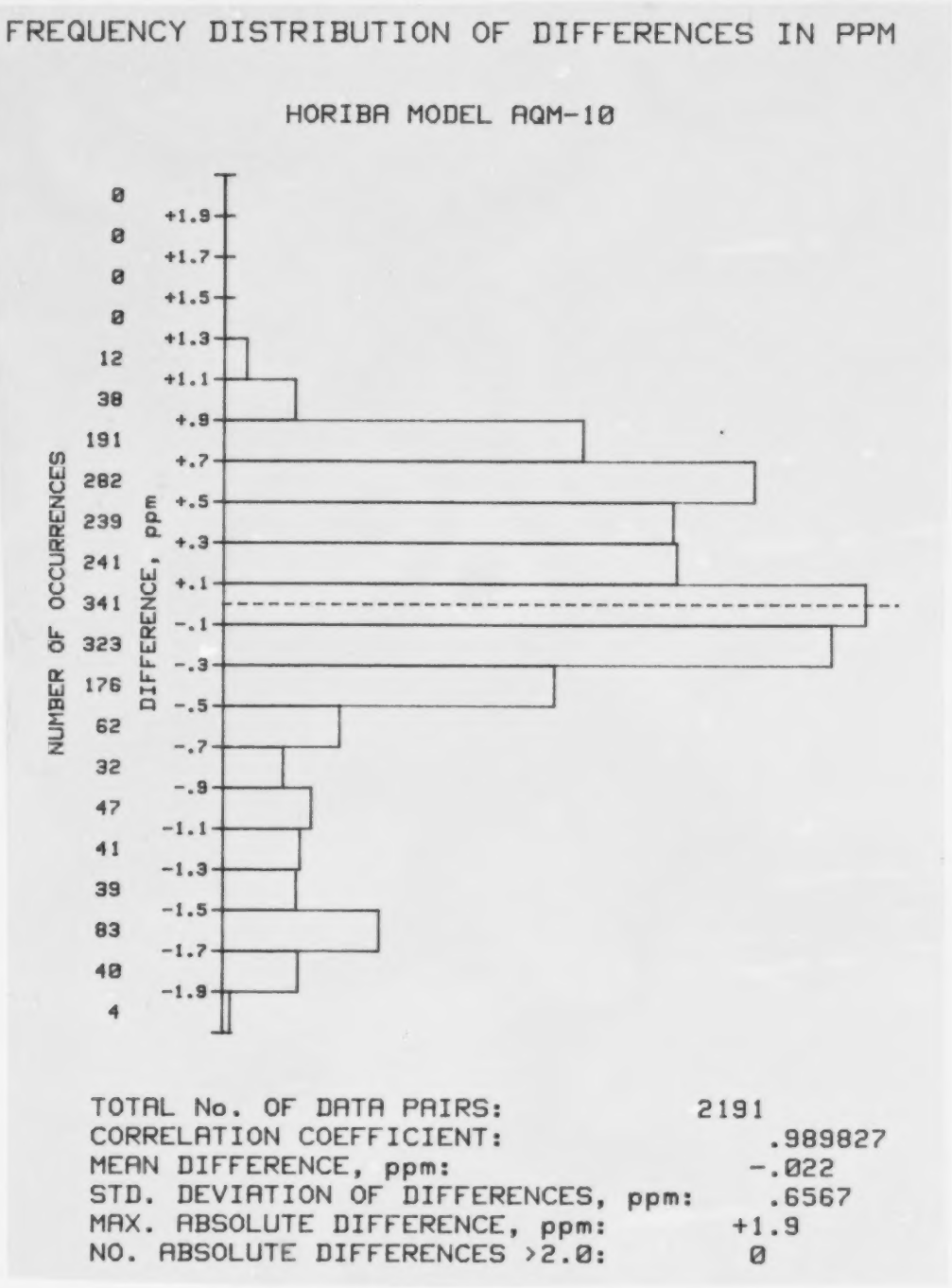


Figure 20. Distribution of differences between the Horiba and the average of the other analyzers during the Phase II ambient monitoring test. Horiba readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Zero and span check.	Weekly.
Optical adjustment.	Semiannually.
Check sample cell and clean or replace.	Yearly.
Replace analyzer gas inlet screen.	Yearly.

Malfunctions

During Phase II testing in June 1980, the analyzer began to exhibit a very large, negative baseline drift (-20 percent of full scale). The optical/electrical alignment procedure described in the operating manual would not correct the problem. Use of a modified alignment procedure (not in the manual) by a factory service representative returned the analyzer to nominal performance.

In July 1980, the analyzer produced a nonlinear calibration curve ($r^2 = 0.9988$). The infrared sources were changed by a factory representative and the nonlinearity was reduced to less than 1 percent full scale at midscale, but not eliminated entirely.

During Phase I testing in January 1981, the analyzer failed 24-hour zero drift, 24-hour 80-percent-of-scale drift, and water vapor interferent tests; see comment below.

General Comments

During Phase I postdesignation testing, this analyzer failed 24-hour zero drift, 24-hour span drift, and water vapor interferent tests. Additionally, a nonlinear calibration curve was noted. The malfunctions seemed to be of two types--those caused by inadequate optical alignment and those caused by shifts in the temperature of air surrounding the analyzer. Problems with nonlinearity in the calibration curve and with water vapor interference seemed to be related to inadequate optical alignment procedures. The drift problems were associated with changes in the ambient temperature surrounding the analyzer.

The analyzer was returned to the Horiba facility in Irvine, California, and investigated to characterize the cause of and to formulate the resolution for these problems. The temperature instability problems were traced to a thermal insulator at the detector heating blocks. Removal of the insulator improved temperature regulation by a factor of 4. Problems with the published optical alignment procedure were traced to a significant shift in alignment parameters that occurred after the alignment procedure

was complete. The shift was caused by the replacement of the optical bench cover and the subsequent increase in bench temperature. The optical alignment procedure was revised to compensate for the difference between alignment parameters with the bench cover on and off. Horiba personnel anticipate distribution of the modified procedure to users of the AQM-10, -11, and -12 shortly.

Before the factory investigation was completed, Horiba personnel repeated those portions of the Phase I postdesignation test that were failed during the original test. The analyzer performed satisfactorily for all test parameters. The data presented in Table 7 are a combination of those from successful portions of the original test and those from the manufacturer-repeated portions of the test. EPA believes these data support the continued designation of this analyzer as a reference method for CO.

For most of the Phase II test, the AIC unit was energized but not engaged. The AIC was engaged for about 3 weeks during September 1980, at which time it was programmed to conduct zero/span operations once every 12 hours--at noon and at midnight. The zero/span sequence was to sample zero air for 2 minutes, adjust zero response for 30 seconds, sample span gas for 2 minutes, adjust span response for 30 seconds, and return to ambient air sampling while inhibiting data acquisition for an additional 2 minutes.

Test data show no significant difference in analyzer performance when the AIC is engaged and when it is not. This result was expected, however, since manual zero/span operations were conducted three times per week throughout the test. The operating manual specifies that "use of the AIC option is recommended only in those cases where the analyzer is to be left unattended for longer than seven (7) days."

During all Phase I testing, the AIC unit was energized but was not engaged.

MASS-CO, MODEL 1

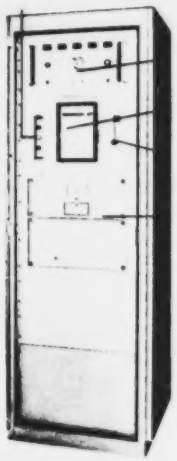


Figure 21. MASS-CO, Model 1 CO analyzer (RFCA-1280-050). Commonwealth of Massachusetts, Department of Environmental Quality Engineering, Tewksbury, Massachusetts 01876.

General Description

The MASS-CO, Model 1 carbon monoxide analyzer operates on the principle of nondispersive infrared spectroscopy described in Appendix A. This analyzer was designated for use within the borders of the Commonwealth of Massachusetts. The method is not currently commercially available. At this time no postdesignation testing has been performed on this method nor is any anticipated in the future.

TABLE 8. MASS-CO, MODEL 1 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.50	0.089	
Noise – 80% URL	ppm	0.50	0.100	
Lower detectable limit	ppm	1.0	0.8	
Interferents	ppm			NO
CO_2		±1.0	0.4	TESTING
H_2O		±1.0	0.4	ANTICIPATED
Total interferents		±1.5	0.8[d]	
Zero drift – 12 h	ppm	±1.0	0.61	
Zero drift – 24 h	ppm	±1.0	0.66[d]	
Span drift – 20% URL	%	±10.0	4.11[d]	
Span drift – 80% URL	%	±2.5	1.09[d]	
Lag time	min	10	0.33	
Rise time	min	5	0.50	
Fall time	min	5	0.56	
Precision – 20% URL	ppm	0.5	0.07	
Precision – 80% URL	ppm	0.5	0.23	

[a]From EPA equivalency regulations, 40 CFR Part 53.

[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests.

[d]Average of absolute values.

MONITOR LABS MODEL 8310

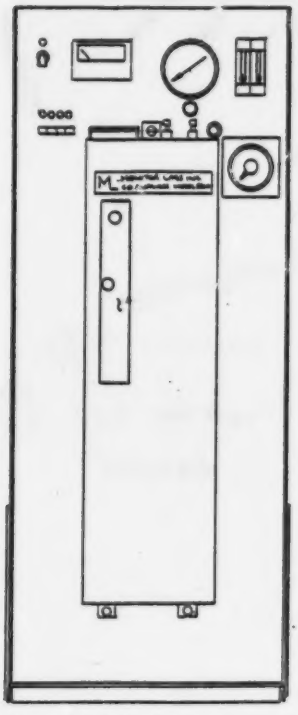


Figure 22. Monitor Labs Model 8310 CO analyzer (RFCA-0979-041). Monitor Labs, Incorporated, 10180 Scripps Ranch Boulevard, San Diego, California 92131.

General Description

The Monitor Labs 8310 carbon monoxide analyzer operates on the principle of nondispersive infrared spectroscopy described in Appendix A. It is equipped with both a flowing sample cell and a flowing reference cell. Carbon-monoxide-free air is provided for the reference cell by passing a portion of the sample through a CO-to-CO_2 converter prior to its introduction into the cell. The infrared energy for both cells is provided by a single source that is split into two equal beams by a beam splitter. Since the beam splitter is filled with 100 percent CO_2, it also performs the function of removing all IR radiation at wavelengths sensitive to CO_2, thus eliminating any CO_2 interference. The analyzer is equipped with an unusual type of detector that uses miniature mass flowmeters to sense the tiny flow between detector chambers caused by differences between sample side and reference side pressures. A major advantage is this type of detector's insensitivity to vibration. Interference from sample water vapor is minimized by use of the flowing reference cell and by use of double reference and sample chambers within the detector.

To be used as a reference analyzer, the 8310 must be operated on the 0-to-50-ppm range and must be equipped with a sample inlet filter. The temperature of the air surrounding the analyzer must remain in the range of 20° to 30° C; the line voltage to the analyzer must be in the range of 105 to 125 Vac. The analyzer may be operated with or without any of the following options:

- Zero/span valves
- Floor stand
- 60-Hz pump
- 50-Hz pump
- CO regulator
- CO cylinder
- Zero/span valve
- Power supply
- Calibration valves
- Special input power transformer.

TABLE 9. MONITOR LABS 8310 LABORATORY PERFORMANCE TEST RESULTS

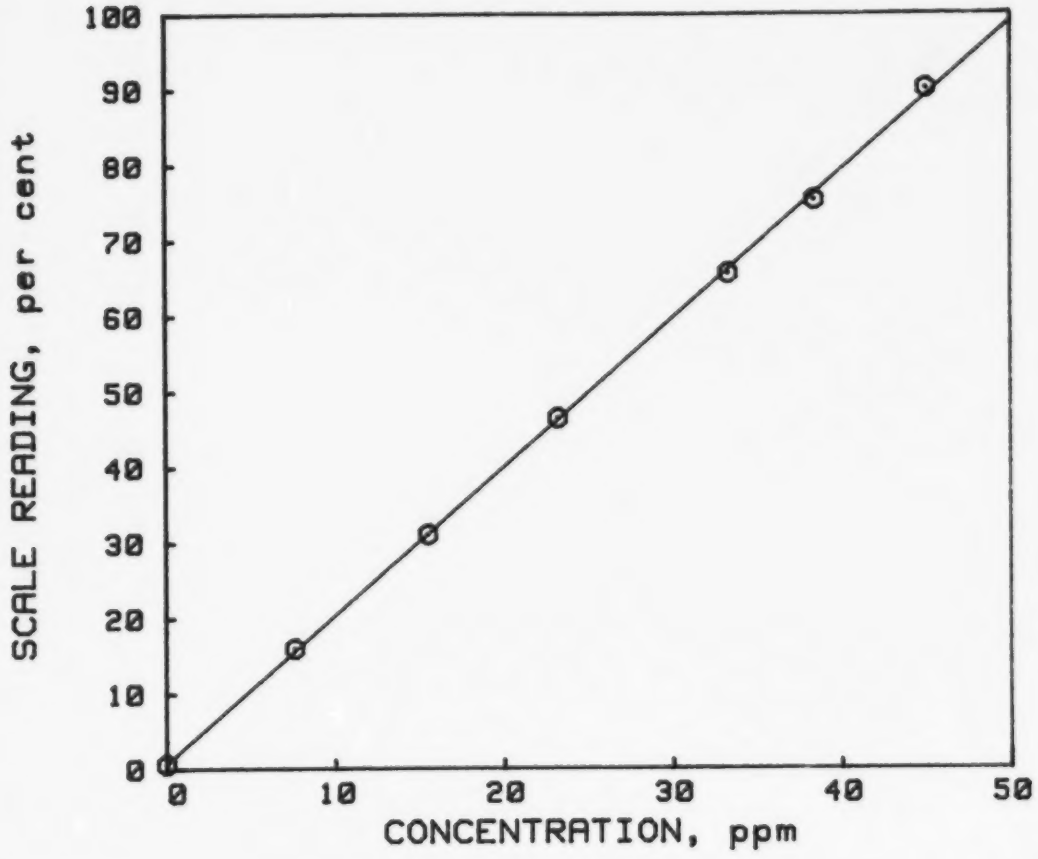
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.50	0.030	0.016
Noise – 80% URL	ppm	0.50	0.066	0.055
Lower detectable limit	ppm	1.0	1.04	1.00
Interferents	ppm			
CO_2		±1.0	-0.05	-0.01
H_2O		±1.0	-0.19	-0.23
Total interferents		±1.5	0.25[d]	0.24[d]
Zero drift – 12 h	ppm	±1.0	0.11	0.30
Zero drift – 24 h	ppm	±1.0	0.14[d]	0.33[d]
Span drift – 20% URL	%	±10.0	1.03[d]	2.34[d]
Span drift – 80% URL	%	±2.5	0.92[d]	0.82[d]
Lag time	min	10	0.2	0.3
Rise time	min	5	0.4	0.7
Fall time	min	5	0.6	0.5
Precision – 20% URL	ppm	0.5	0.05	0.022
Precision – 80% URL	ppm	0.5	0.04	0.104

[a]From EPA equivalency regulations, 40 CFR Part 53.

[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests, serial number NOA1188T.

[d]Average of absolute values.



ANALYZER:	MONITOR LABS	Y = MX + A	DATA:	X	Y
MODEL:	8310		1	0.000	.600
SERIAL No.:	NOA1188T	M = 1.965	2	7.600	16.000
POLLUTANT:	CO	95% C.I.= ± .042	3	15.500	31.100
RANGE:	50 ppm		4	23.200	46.500
LOCATION:	DAMDF	A = .702	5	33.300	65.600
DATE:	09/03/80	95% C.I.= ± 1.161	6	38.400	75.300
DATE CODE:	80.247		7	45.000	90.100
NAME:	PHASE II	r = .99983			

Figure 23. Typical calibration curve for Monitor Labs 8310.

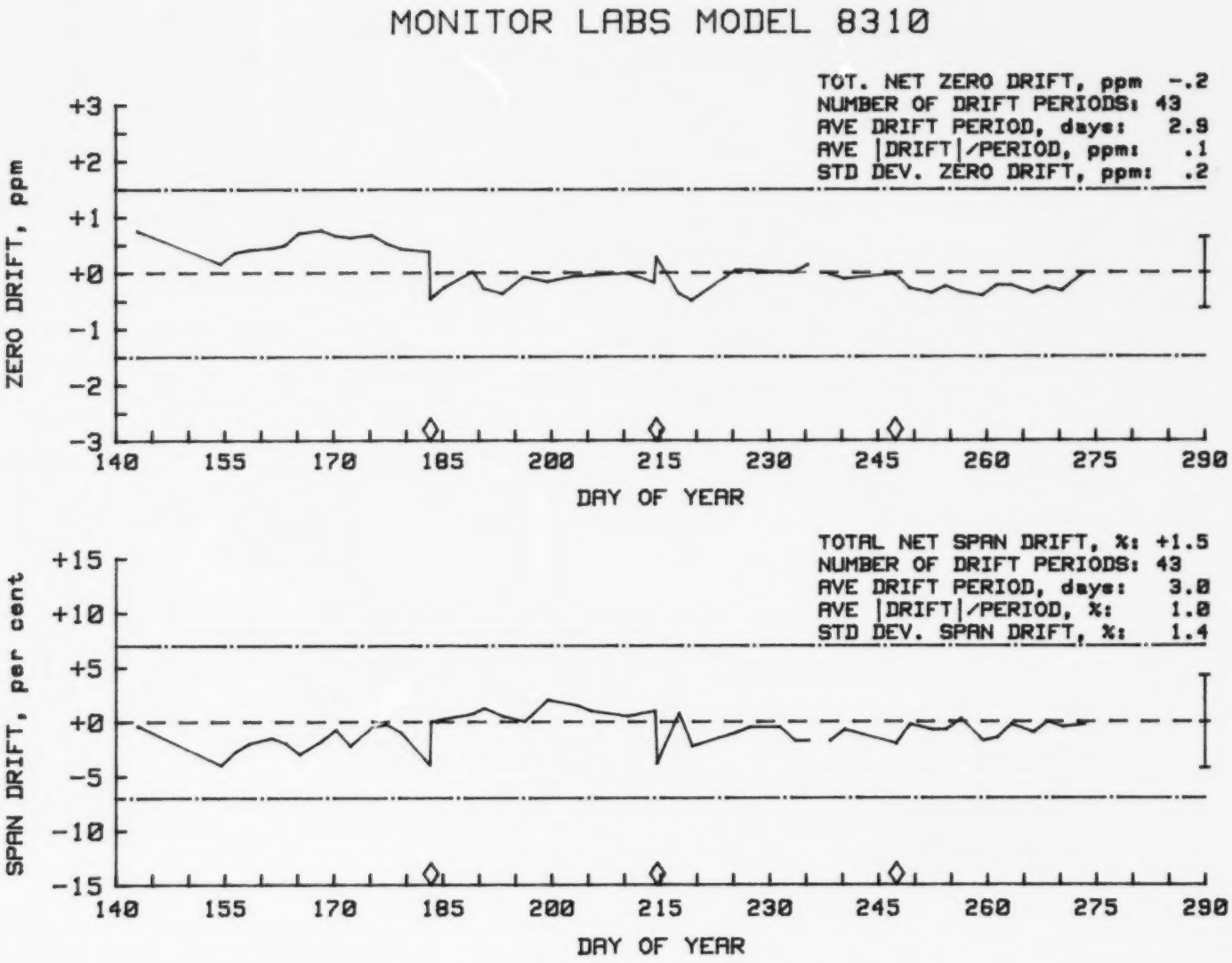


Figure 24. Zero and span drift for Monitor Labs analyzer during Phase II testing.

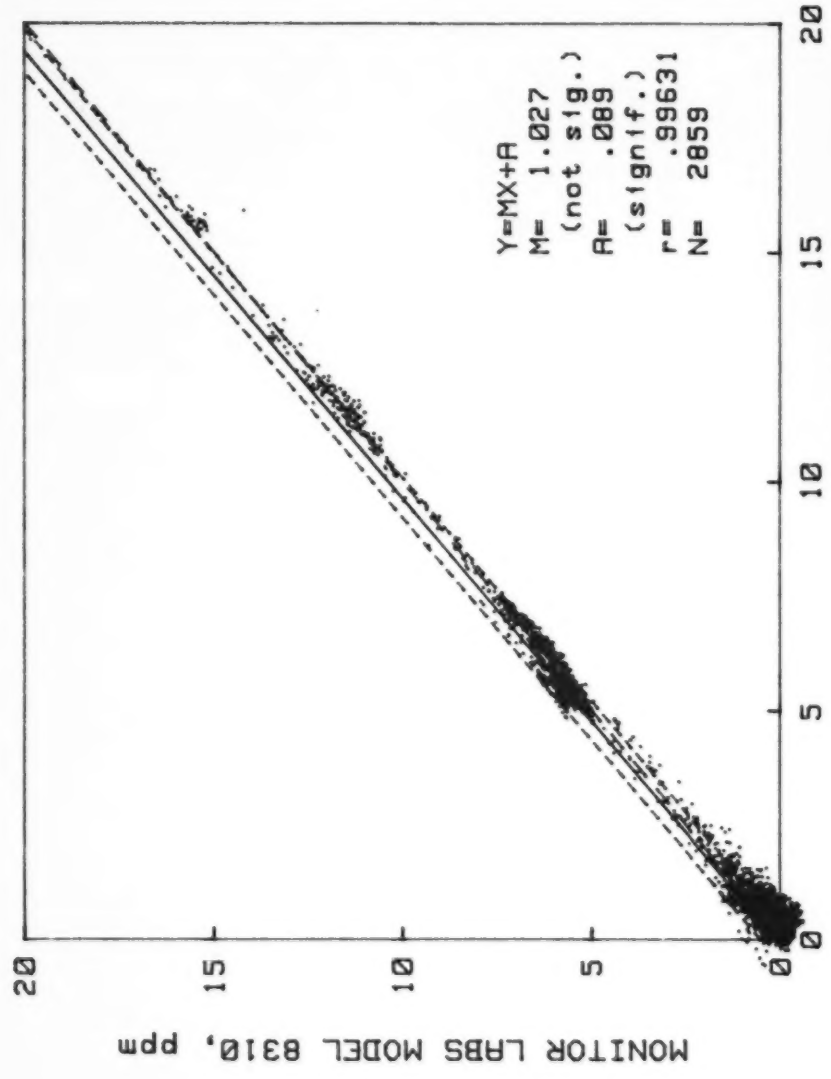


Figure 25. Correlation between the Monitor Labs and the average of the other analyzers during the Phase II ambient monitoring test.

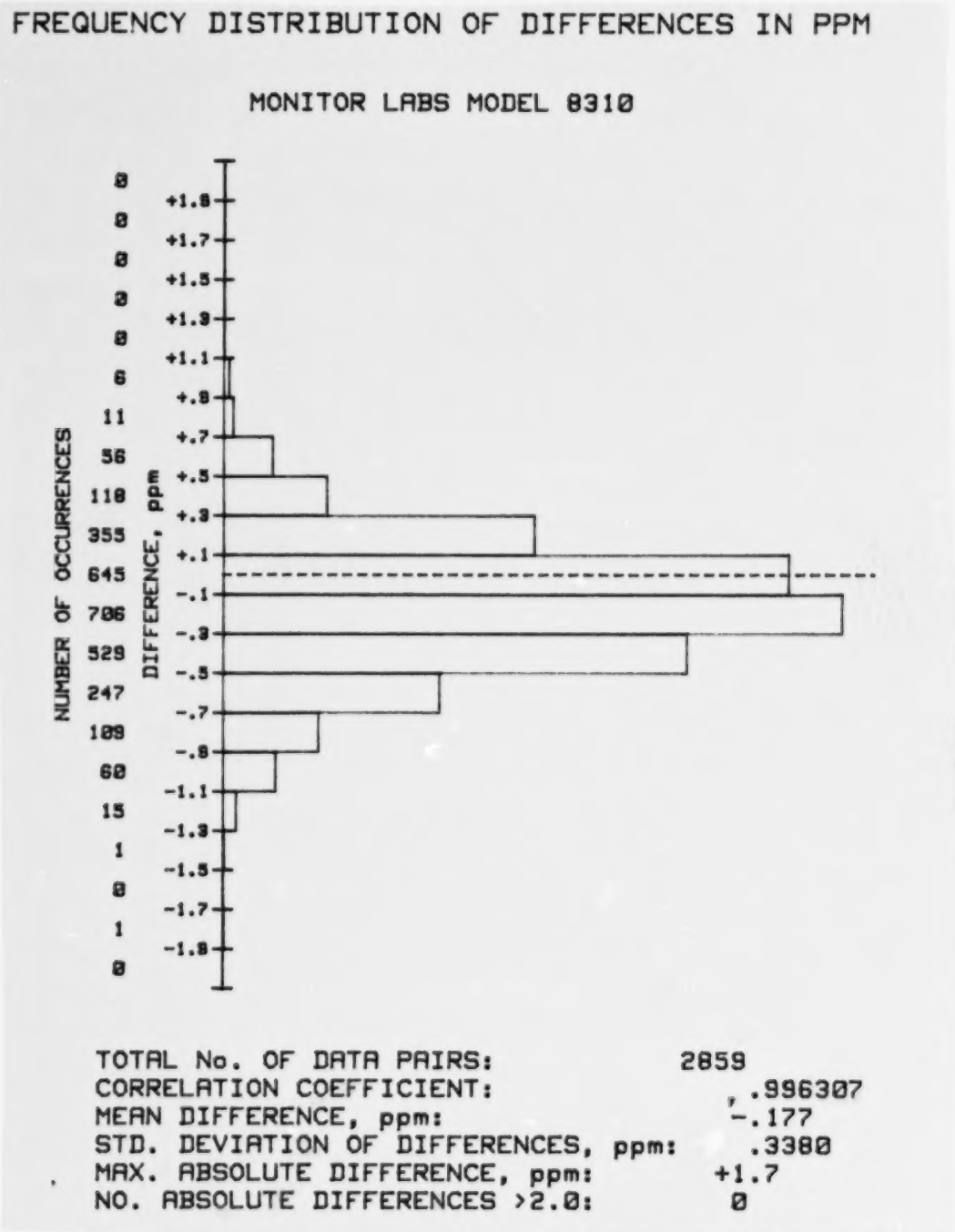


Figure 26. Distribution of differences between the Monitor Labs and the average of the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

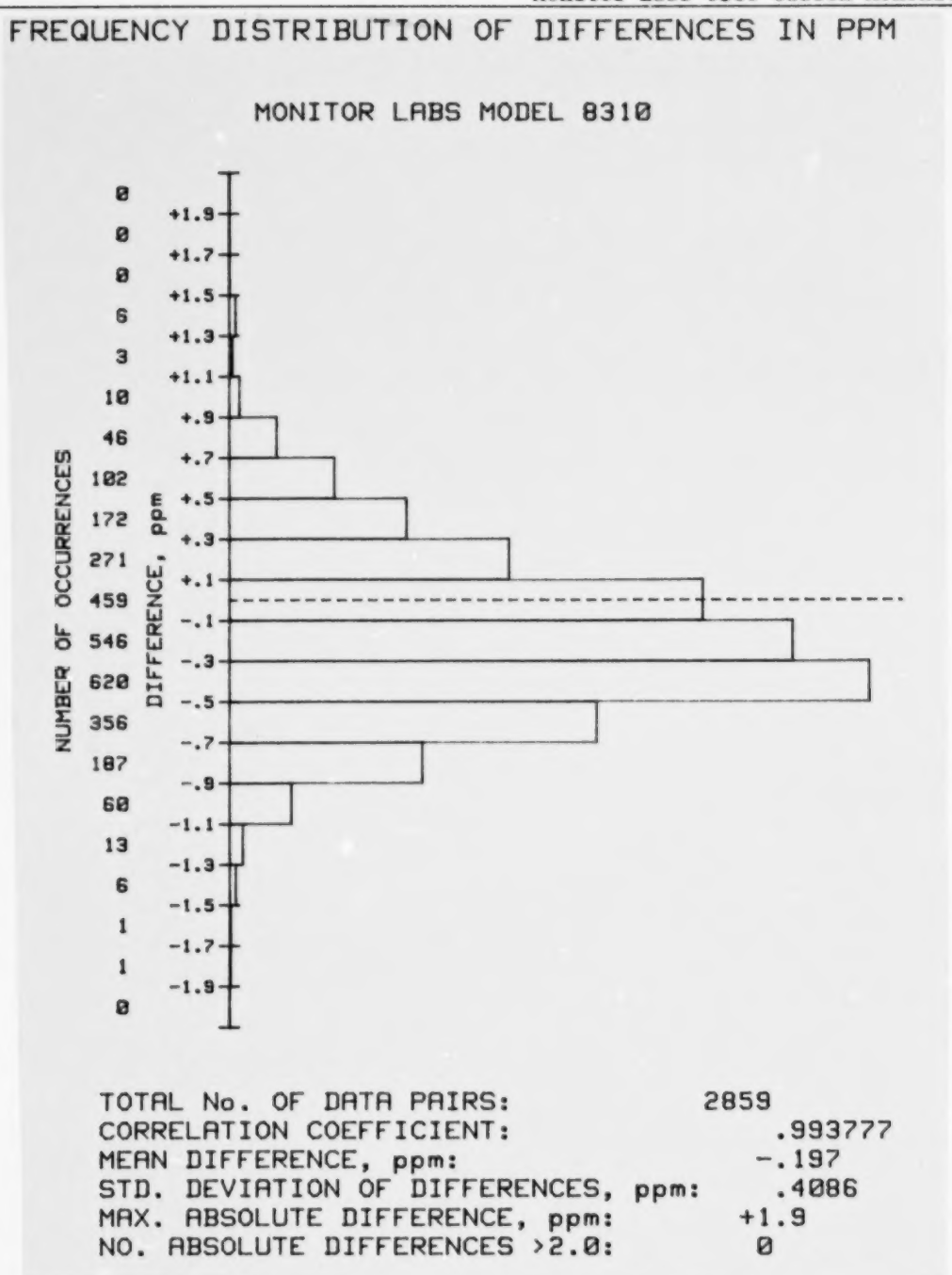


Figure 27. Distribution of differences between the Monitor Labs and the average of the other analyzers during the Phase II ambient monitoring test. Monitor Labs readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Check sample filter.	Weekly.
Check flow control orifices.	Weekly.
Check pump.	Weekly.
Replace sample filter.	Monthly.
Clean flow control orifices.	As required.
Replace sample pump.	As required.
Replace CO-to-CO_2 converter.	Semiannually.
Check flow cells.	As required.
Replace span gas cylinder.	As required.

Malfunctions

No malfunctions were experienced throughout Phase I or Phase II testing.

General Comments

Phase I testing was conducted in January 1981. Phase II testing was conducted from May through September 1980.

MSA LIRA MODEL 202S

Figure 28. MSA LIRA Model 202S air quality carbon monoxide analyzer system (RFCA-0177-018). Mine Safety Appliance Company, 600 Penn Center Boulevard, Pittsburgh, Pennsylvania 15208.

General Description

The MSA LIRA 202S air quality carbon monoxide analyzer system operates on the principle of nondispersive infrared spectroscopy described in Appendix A. It is equipped with a flowing sample cell and a sealed reference cell. The detector is of the Luft type. This analyzer features a sample cell that operates at a pressure of 103 kPa (15 psig) to increase the sensitivity of the system. The elevated pressure in the cell is produced by initially compressing the sample gas to 240 to 275 kPa (35-40 psig), then successively reducing that pressure to the 103-kPa level. These elevated sample pressures necessitate an efficient method of sample water removal, which is accomplished by a coalescing filter, a heatless MSA regenerative dryer, and successive sample pressure reductions performed concurrently with the mechanical drying steps. This drying of the sample gas also effectively minimizes the interference of sample water vapor during the measurement of CO. The minimization of interference by other species in the sample matrix (e.g., CO_2) is accomplished by passing the IR radiation destined for the sample cell through a filter cell first. This filter cell is sealed and contains gases that absorb portions of the incident radiation spectrum representing potential interfering species.

To be used as a reference analyzer, the LIRA 202S must be operated on the 0-to-50-ppm range with the "slow response" amplifier. Use of the sample inlet filter is required. The analyzer may be operated with any of five voltage or seven milliamperage output ranges. Ambient temperature surrounding the analyzer must be in the range of 20° to 30° C; line voltage to the analyzer must be in the range of 105 to 125 Vac. The analyzer may be operated with or without the following options:

- Remote meter
- Remote zero and span controls.

TABLE 10. MSA LIRA 202S LABORATORY PERFORMANCE TEST RESULTS

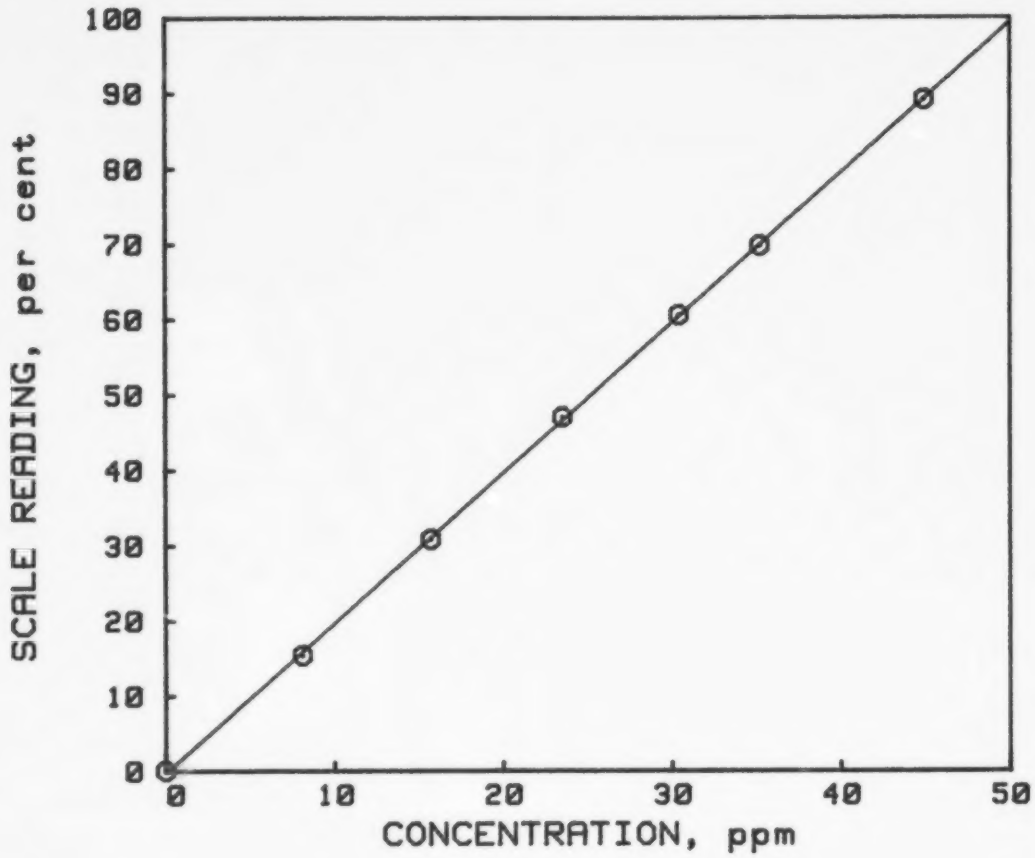
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.50	0.049	0.049
Noise – 80% URL	ppm	0.50	0.049	0.061
Lower detectable limit	ppm	1.0	0.99	1.05
Interferents	ppm			
CO_2		±1.0	0.17	0.11
H_2O		±1.0	0.23	0.20
Total interferents		±1.5	0.40[d]	0.31[d]
Zero drift – 12 h	ppm	±1.0	0.61	0.50
Zero drift – 24 h	ppm	±1.0	0.30[d]	0.25[d]
Span drift – 20% URL	%	±10.0	1.79[d]	2.40[d]
Span drift – 80% URL	%	±2.5	0.45[d]	0.86[d]
Lag time	min	10	0.5	0.4
Rise time	min	5	0.6	0.6
Fall time	min	5	0.8	0.5
Precision – 20% URL	ppm	0.5	0.014	0.055
Precision – 80% URL	ppm	0.5	0.023	0.038

[a]From EPA equivalency regulations, 40 CFR Part 53.

[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests, serial number 21125.

[d]Average of absolute values.



ANALYZER:	MSA	Y = MX + A	DATA:	X	Y
MODEL:	202S				
SERIAL No.:	21125	M = 1.992	1	0.000	0.000
POLLUTANT:	CO	95% C.I.= ± .023	2	8.100	15.400
RANGE:	50 ppm		3	15.700	30.800
LOCATION:	DAMDF	A = -.273	4	23.500	47.000
DATE:	05/22/80	95% C.I.= ± .627	5	30.400	60.500
DATE CODE:	80.143		6	35.200	69.700
NAME:	PHASE II	r = .99995	7	44.900	89.100

Figure 29. Typical calibration curve for MSA 202S.

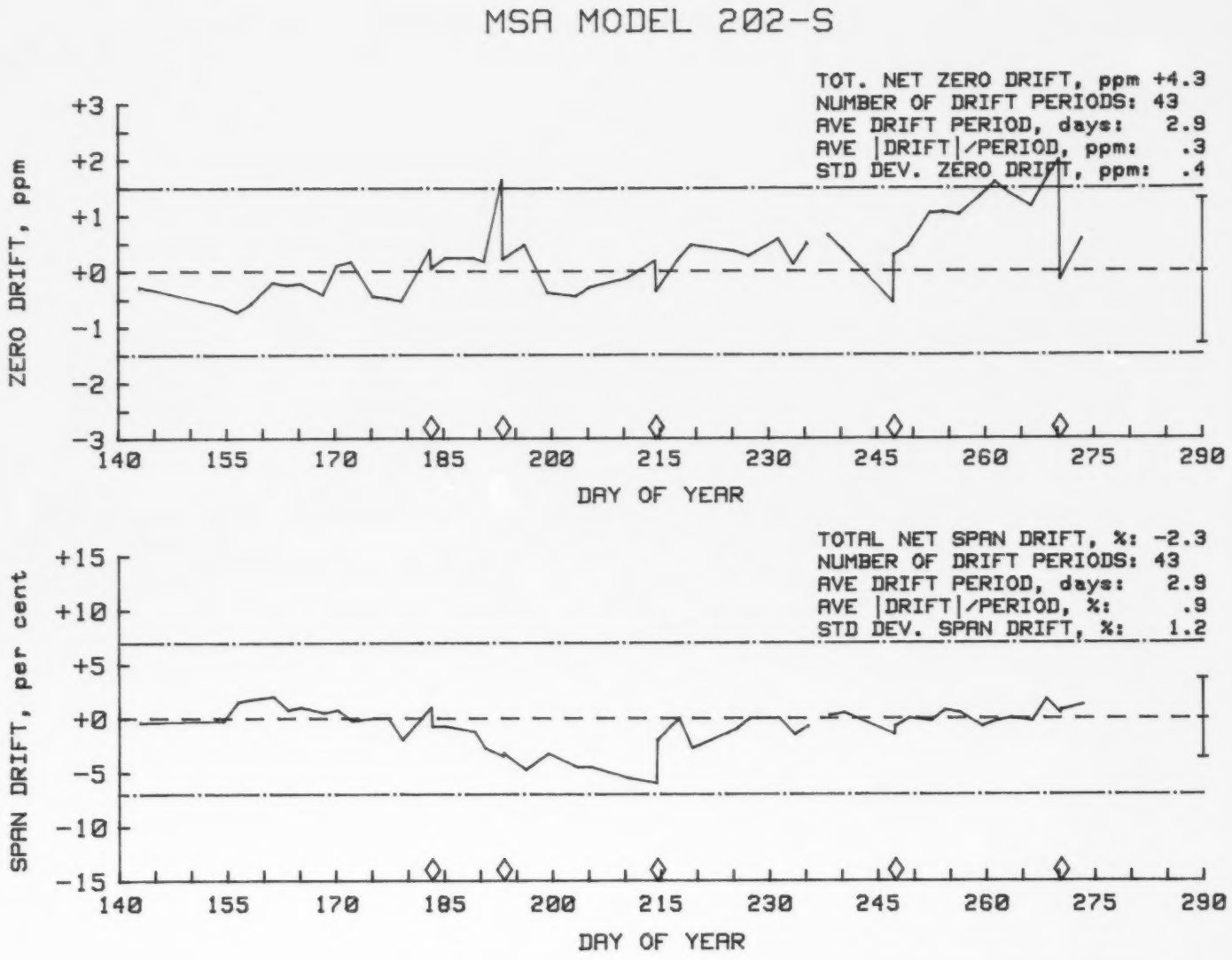


Figure 30. Zero and span drift for MSA analyzer during Phase II testing.

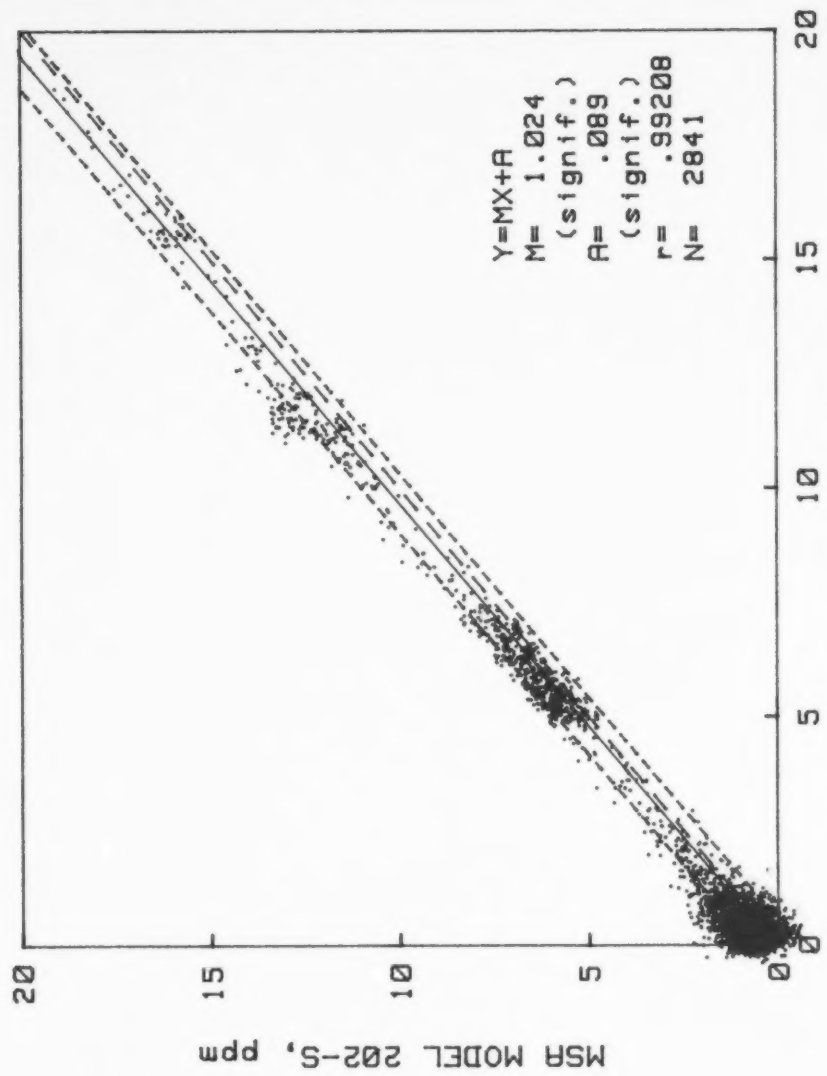
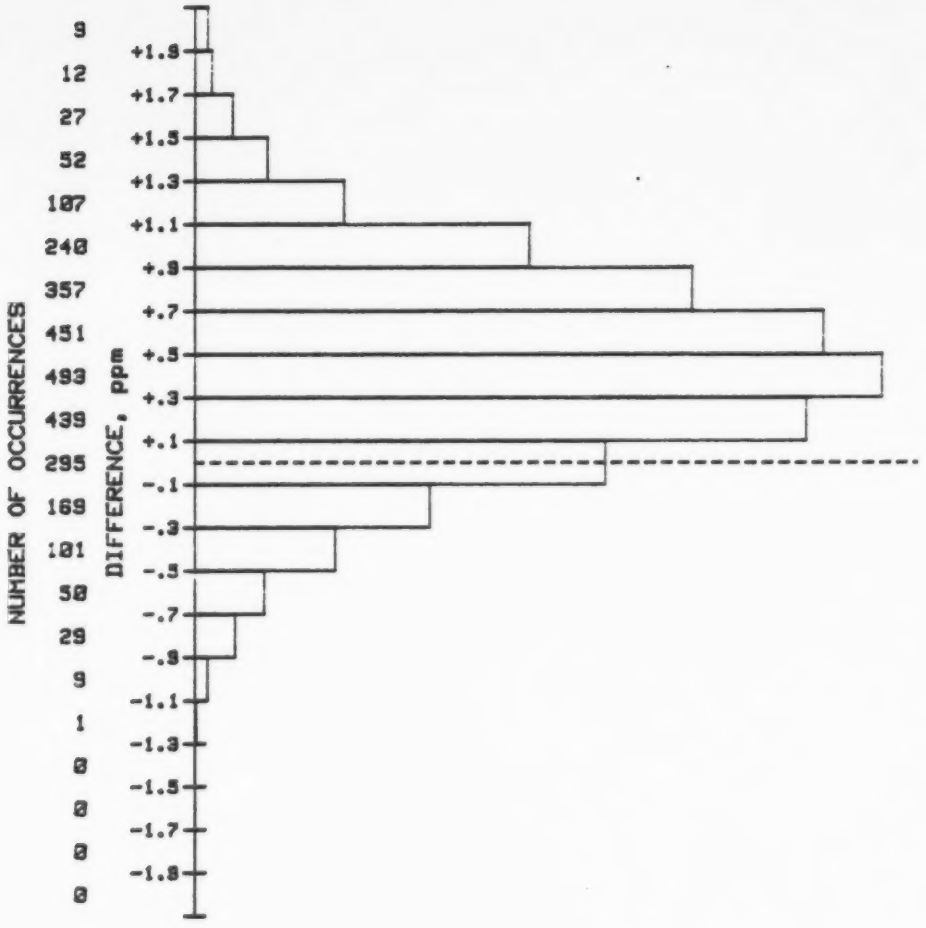


Figure 31. Correlation between the MSA and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPM

MSA MODEL 202-S



TOTAL No. OF DATA PAIRS:	2841
CORRELATION COEFFICIENT:	.992079
MEAN DIFFERENCE, ppm:	+.432
STD. DEVIATION OF DIFFERENCES, ppm:	.4833
MAX. ABSOLUTE DIFFERENCE, ppm:	+2.2
NO. ABSOLUTE DIFFERENCES >2.0:	5

Figure 32. Distribution of differences between the MSA and the average of the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

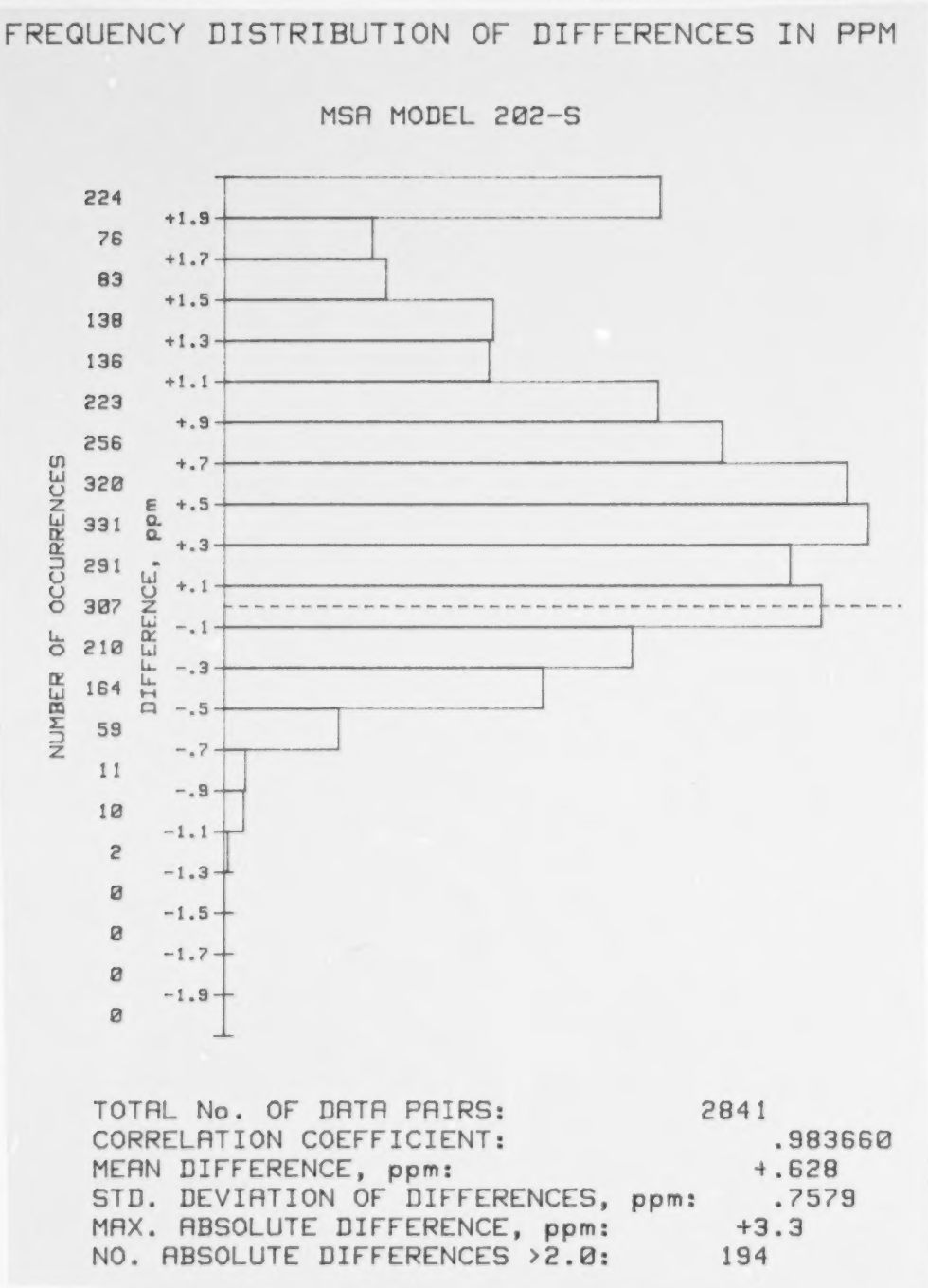


Figure 33. Distribution of differences between the MSA and the average of the other analyzers during the Phase II ambient monitoring test. MSA readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Check LIRA cell pressure gauge.	Twice per week.
Check cell flow rotameter.	Twice per week.
Check/reset cell pressure regulator.	As necessary.
Drain water from coalescing filter.	As necessary.
Check sample pump performance.	As necessary.
Check sample inlet filter.	Monthly.
Replace coalescing filter drain fitting.	Monthly.
Replace coalescing filter internal element.	Monthly.

Malfunctions

No malfunctions were experienced throughout Phase I or Phase II testing.

General Comments

Prior to Phase I testing, zero-level signal noise was excessive during an initial calibration. Following the alignment of the optical bench by a factory representative, the noise level decreased by a factor of three. It was assumed that the optical bench had become misaligned during shipment.

During Phase II testing, it was noted that a good seal was not always achieved around the MSA cartridge filter housing after filter replacement. A poor seal results in a leak in the sample path, which, because the path is under reduced pressure at that point, results in a dilution of the sample. It is recommended that a span level check be performed after filter replacement. An abnormally low span response may be due to a leak in the filter housing.

THERMO ELECTRON MODEL 48

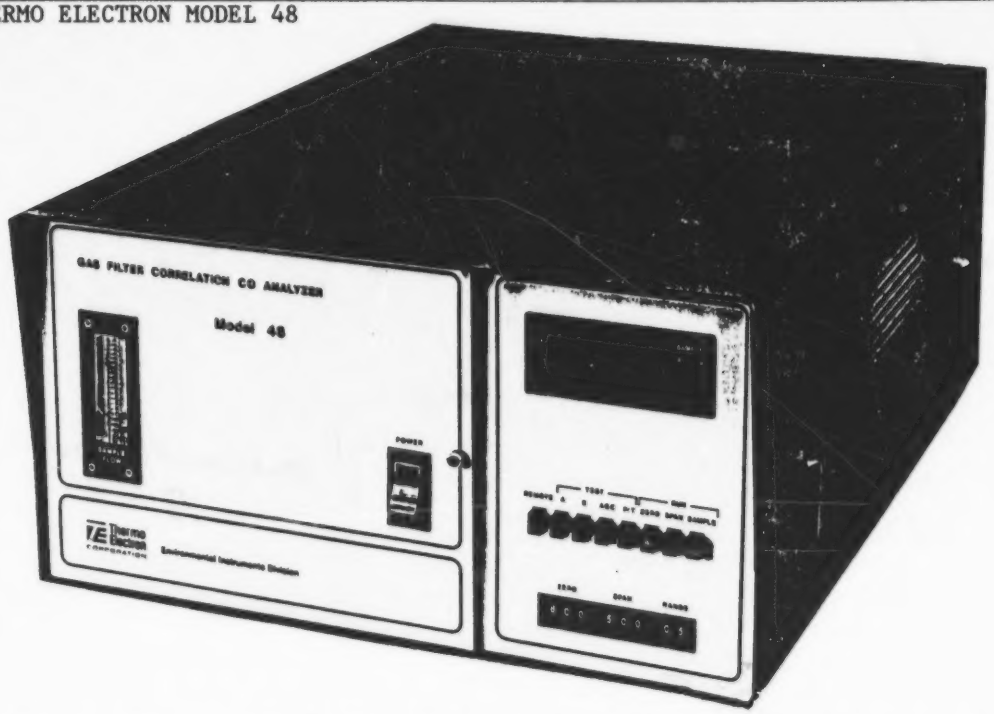


Figure 34. Thermo Electron Model 48 gas filter correlation ambient CO analyzer (RFCA-0981-054). Thermo Electron Corporation, Environmental Instruments Division, 108 South Street, Hopkinton, Massachusetts 01748.

General Description

The Thermo Electron Model 48 gas filter correlation ambient CO analyzer operates on the principle of gas filter correlation NDIR spectroscopy described in Appendix A. It is equipped with a solid-state detector and multiple pass optics in the sample cell. The effects of interfering species on the measurement are minimized by the nature of the GFC technique itself.

To be used as a reference analyzer, the Model 48 must be operated on the 0-to-50-ppm range with a time constant setting of 30 seconds. Ambient temperature surrounding the analyzer must be in the range of 20° to 30° C; line voltage to the analyzer must be in the range of 105 to 125 Vac. The analyzer may be used with or without any of the following options:

- Particulate filter
- 19-Inch rack-mountable configuration
- Remote activation of zero and span
- Internal zero air package
- GPIB (general purpose interface bus) IEEE-488.

TABLE 11. THERMO ELECTRON 48 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise–0% URL	ppm	0.50	0.027	0.027
Noise–80% URL	ppm	0.50	0.063	0.053
Lower detectable limit	ppm	1.0	0.65	1.02
Interferents	ppm			
CO_2		±1.0	>-0.01	0.20
H_2O		±1.0	0.05	-0.04
Total interferents		±1.5	0.06[d]	0.24[d]
Zero drift–12 h	ppm	±1.0	0.09	0.11
Zero drift–24 h	ppm	±1.0	0.06[d]	0.04[d]
Span drift–20% URL	%	±10.0	1.24[d]	0.86[d]
Span drift–80% URL	%	±2.5	0.91[d]	0.69[d]
Lag time	min	10	0.4	<0.2
Rise time	min	5	1.3	0.8
Fall time	min	5	1.3	1.0
Precision–20% URL	ppm	0.5	0.009	0.039
Precision–80% URL	ppm	0.5	0.029	0.031

[a]From EPA equivalency regulations, 40 CFR Part 53.

[b]Average, from manufacturer's application for equivalency determination.

[c]Average, from EPA Phase I postdesignation tests, serial number ACM-13129-134.

[d]Average of absolute values.

Manufacturer's Recommended Maintenance

Operation	Frequency
Clean optical bench.	Prior to recalibration.
Replace source.	Annually.
Check detector frequencies.	Periodically.*
Calibrate pressure transducer.	Periodically.*
Calibrate temperature transducer.	Periodically.*
Check for leaks and pump condition.	Periodically.*
Check/adjust D/A converter.	Periodically.*

Malfunctions

No malfunctions were noted throughout Phase I testing.

General Comments

Phase I testing was conducted in June 1982. Phase II testing has not been conducted as of this writing.

*Operating manual specifies "checking . . . should be . . . performed on a regular basis."

APPENDIX A

MEASUREMENT PRINCIPLE FOR CARBON MONOXIDE ANALYZERS

All EPA-designated carbon monoxide analyzers designated to date are reference methods and accordingly employ the measurement principle specified in Appendix C of 40 CFR Part 50, Nondispersive Infrared Spectroscopy. This principle is described in this section to enhance the reader's understanding of the analyzers.

Conventional Nondispersive Infrared Spectroscopy

Gas molecules containing two or more dissimilar atoms absorb energy at particular wavelengths in the infrared (IR) portion of the electromagnetic spectrum. The pattern of IR wavelengths absorbed by a molecule is characteristic of that molecule only and is known as the absorption spectrum of the molecule. The characteristic absorption spectrum of the carbon monoxide (CO) molecule is centered around a wavelength of 4.6 μm and is the basis for its detection and quantification by nondispersive infrared (NDIR) spectroscopy.

Infrared spectroscopy may be either dispersive or nondispersive. In dispersive spectroscopy, a prism or diffraction grating is employed between the IR radiation source and the sample. The effect of this prism or grating is to select a very narrow wavelength band of radiation for passage through the sample. In essence, this narrow wavelength band can be thought of as a "single wavelength" of radiation. This technique of wavelength selection is used most often in high precision laboratory instruments because the prisms and gratings are expensive, delicate, and must be aligned very precisely.

Nondispersive spectroscopy, conversely, utilizes no prism or grating to disperse the source radiation and is the technique employed in ambient CO analyzers. The wavelengths of interest are selected from the source by a nondispersive technique such as optical filtering, often employing the gas to be measured as the filtering medium.

All NDIR CO analyzers consist of at least three basic sections: a source of IR radiation, sample and reference cells, and an IR radiation detector. The source of radiation is usually a glowing wire, similar to an ordinary light bulb. Currently designated analyzers contain one of two source configurations. One configuration consists of a single source whose output is split into two parallel beams of nearly equal energy, one directed into the sample cell and the other into the reference cell. In the second configuration, two separate sources are used, one for the sample cell and one for the reference cell.

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The ambient sample being analyzed is exposed to the source radiation as it flows through the sample cell. The CO-free matrix against which the sample is referenced is contained within the reference cell. The cells are basically identical in construction, consisting of tubes typically 0.5 m in length and capped with IR-transparent windows at both ends. They are optically aligned along their length within the IR radiation beam between the source and the detector. The sample cell is always equipped with an inlet port and an outlet port at opposite ends to allow the sample gas to flow continuously through the cell. The reference may also be a flowing cell or it may be sealed and contain a nonabsorbing gas such as nitrogen. If the reference cell is of the flowing type, the analyzer must be capable of producing CO-free gas for use as the reference matrix. CO-free gas is usually produced by passing the matrix destined for the reference cell (usually a portion of the ambient sample itself) through a catalytic oxidizer capable of oxidizing CO to CO_2. The advantage of a flowing reference cell over a static one is that a flowing cell contains the same matrix as the sample cell, minus CO, which minimizes the effect of potentially interfering species in the sample matrix such as water vapor and CO_2.

There are two types of detectors currently in use in NDIR CO analyzers--the Luft or condenser microphone type and the flow sensing type. These detectors each have two internal chambers, which may or may not be interconnected. In the Luft detector, the chambers are separated by a thin, flexible metal diaphragm. In the flow sensing type, the chambers are connected by a small passage in which a miniature flow sensor is installed. In both types, the chambers are filled with CO to absorb radiation typical of the CO absorption spectrum reaching the detector from the source. The physical configuration of the chambers within the detector with respect to the sample and reference cells varies with analyzer manufacturer. In some analyzers, two independent detectors, each with two internal chambers, are used. The different configurations are simply different concepts for accomplishing detection and dealing with interferences. Specific knowledge of the physical configuration is not essential to an understanding of the general detection principle.

The detection principle is based on the fact that IR radiation reaching the detector chambers is absorbed, causing heating of the gas within the chamber. This heating, in turn, causes gas expansion or pressure increase within the chamber. If equal radiation reaches both chambers within the detector, the expansion or pressure increase in both chambers will be equal, such as is the case when there is no CO present in the analyzed sample. When CO is present in the sample cell, unequal amounts of radiation will reach the detector chambers, causing a pressure imbalance within the detector. When this occurs within a Luft detector, the metal diaphragm separating the two chambers distorts or distends toward the chamber with lower pressure. The diaphragm is used as one plate of a variable capacitor in a tank circuit within the analyzer electronics. Distension of the diaphragm changes the capacitance, shifting the resonance frequency of the circuit. This frequency shift is processed by the electronics into a

voltage or current proportional to the concentration of CO in the sample stream. In the flow-sensing detector, the pressure imbalance between detector chambers induces gas flow through the passage connecting the chambers. This flow is detected by the flow sensor, which produces a signal that can be processed by the electronics into a suitable output signal. In most currently designated CO analyzers, the IR radiation is mechanically "chopped" prior to its reaching the detector. The chopping is accomplished using a fan-blade-like chopper, which alternately blocks and passes the radiation, producing a beam that is typically modulated at a frequency of 2 to 10 Hz. Therefore, the output from the detector is also modulated at the chopping frequency, which produces a signal that is more easily processed by the electronics package.

Gas Filter Correlation Spectroscopy

Recently, several analyzers have been designated that utilize a modification of the conventional NDIR technique as their principle of measurement. This technique, called gas filter correlation (GFC) spectroscopy, is so closely allied with NDIR spectroscopy that both are considered a part of the same measurement principle. Thus, analyzers utilizing the GFC technique are also considered reference methods for CO.

GFC spectroscopy depends on the absorption of IR radiation in the spectral region of 4.6 μm as does NDIR spectroscopy. The GFC technique is also nondispersive in nature, depending on optical filtering for the selection of appropriate radiation bandwidth. However, a distinguishing feature of GFC is that the optical filter is independent from the detector and is contained in a rotating wheel so that no reference cell is required. Radiation from a single IR source is directed upon the rotating wheel, which contains two IR-transparent gas filter cells. One cell contains nitrogen, which absorbs no radiation; the other contains a high concentration of CO, which absorbs all frequencies in the incident radiation characteristic of the CO absorption spectrum. After passage through these gas cells, the N_2-filtered beam and the CO-filtered beam are unequal in overall (total spectrum) energy. This is due to removal of energy by the filtering effect of the CO cell. This imbalance is compensated for by neutral density filtering of the N_2-filtered beam or other means so that the energy entering the sample cell is essentially constant, either from the N_2-filtering cell or from the CO-filtering cell. The important property of this radiation is that the portion from the N_2 cell continues to contain frequencies subject to absorption by CO while the portion from the CO cell does not.

After passage through the single, flowing sample cell, the IR radiation is directed to a single IR detector. When no CO is present in the sample cell, the IR energy reaching the detector is equal during both halves of the N_2/CO filtering cycle. If an interfering compound (e.g., $H_2O(v)$ or CO_2) is present in the sample matrix, both the N_2-filtered and the CO-filtered radiation will be reduced in energy by an essentially equal amount. Therefore, the analyzer electronics will detect no energy difference in the

two halves of the cycle and will register no output. If, however, CO is present in the sample cell, a reduction in radiation intensity will occur during the N_2-filtered portion of the cycle due to absorption by the CO in the sample. The radiation intensity from the CO-filtered portion of the cycle, no longer sensitive to CO, will experience no reduction in energy. Thus, an intensity difference between the two cycle halves will be sensed at the detector and the analyzer will output a signal proportional to the concentration of CO in the sample.

Because the optical filtering is independent from the detector, a simple, wide-band, solid-state detector can be used. Also, no reference cell is required. It is therefore possible to greatly enhance the sensitivity of the analysis by using multiple pass optics in the sample cell. This multiple pass technique allows a long optical pathlength (and thus good sensitivity) in a sample cell of small physical size.

Another feature of GFC analyzers is that the use of solid-state detectors eliminates the vibration sensitivity problems associated with Luft-type detectors.

Points to Consider When Monitoring CO by IR Spectroscopy

Several points must be remembered when infrared spectroscopy (either NDIR or GFC) is used to measure ambient CO. First, the IR analysis principle is based on the absorption of infrared energy or heat. It is, therefore, extremely important to maintain a constant temperature around the detector. Fluctuations in the temperature surrounding the detector could appear as apparent drift in the output signal. Currently designated analyzers are equipped either to maintain a constant temperature (typically 50° C) around the optical bench or to compensate electronically for temperature variations around the bench. It is important that users maintain this temperature control/compensation system in good condition. It is also important that the analyzer be operated with all optical bench covers in place and with all access doors to the bench closed.

It is also important to remember that carbon dioxide (CO_2) and water vapor are potential interferents in infrared spectroscopic analysis of CO because they both absorb IR radiation in the same spectral region as CO. Many design features are incorporated into these analyzers to minimize the effects of these species, including flowing reference cells, optical filters, gas-filled filters, multiple detectors, and CO_2-filled beam splitters. However, the user should be aware that these interferences exist and should seek to minimize their effect wherever possible. It is generally considered good monitoring practice to maintain ambient levels of carbon dioxide in zero and calibration gases. This can be accomplished by drawing air for zero air systems from a source outside of any building and by utilizing a chemical scrubbing system that does not remove CO_2. Ambient levels of CO_2 in zero and calibration gases minimize the occurrence of CO_2 interference because of differences in sample and calibration matrix CO_2 concentrations.

The inclusion of ambient levels of water vapor in zero and calibration gases is usually not recommended. Therefore, the occurrence of a water vapor concentration difference between sample and calibration matrices is unavoidable. Both field and laboratory experience have shown that all currently designated CO analyzers are capable of correcting for the difference between a "dry" calibration matrix and a "wet" sample matrix. Compensation difficulties have been noted in certain analyzers, however, during the transition between wet and dry states or vice versa. The transition period is characterized by a slow drift in the output signal that may last as long as an hour and span up to 5 percent of full scale. Adequate time must be allowed for the completion of the transition period before calibration data are recorded to ensure that this interference does not result in invalid data. Following calibrations, a similar delay should be observed before ambient measurements are recorded.